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THE CHEMISTRY OF ACETYLENE AND RELATED COMPOUNDS

POLYTECHNIC INSTITUTE OF BROOKLYN

LECTURES ON PROGRESS IN CHEMISTRY

EDITOR: H. MARK

INSTITUTE OF POLYMER RESEARCH

THE CHEMISTRY OF ACETYLENE AND RELATED COMPOUNDS

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REHOVOT, PALESTINE

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To my future colleagues
at the Weizmann Institute of Science
in anticipation of fruitful joint
research in the service of our country

PREFACE

Recent events in petroleum politics have focused attention once again on coal as a possible fundamental raw material. With the development of new processes that will break the traditional association of coal with aromatic compounds, considerable attention has been given to acetylene as a most versatile starting material available from coal. My interest in the chemistry of acetylene was enhanced by the work of Dr. Chaim Weizmann and his collaborators, who devoted a great deal of study to it following an important observation made by my friends, the late Dr. J. Zeltner and Dr. M. Genas, in Paris shortly before the Second World War.

Having taken part in this investigation, I was very happy to accept Dr. Mark's invitation to present a seminar on acetylene chemistry at the Polytechnic Institute of Brooklyn in the fall of 1946. It was neither intended nor indeed feasible to survey this vast field completely in the course of three lectures; rather, a general outline was given that emphasized recent developments.

Despite the limitations imposed by confining such a complex field to three lectures, it is nevertheless hoped that this book will be useful to its readers as an introduction to a fascinating and promising domain of organic chemistry, and that the addition of references to the literature will stimulate, and assist in, further studies.

ERNST BERGMANN

February, 1948

FIRST LECTURE

I must apologize for the unforeseen delay of our three seminars on the chemistry of acetylene and related substances. Apparently the validity of the principle of indetermination is not limited to atomic and subatomic phenomena, but is also applicable to the means of transportation and communication. On the other hand, the selection of the subject for these three seminars does not require any explanation. Acetylene, always known as a reactive and versatile substance, has recently attracted an attention that is increasing at the same rate at which the transition of the chemical industry to synthetic products proceeds.

Even from a purely thermochemical standpoint acetylene commands attention. Let us consider its free energy. Its heat of formation according to the equation:[1]

$$2\,\mathrm{C(graphite)} + \mathrm{H_2} = \mathrm{C_2H_2}$$

is:

$$\Delta H_{291} = 54{,}900$$

If we make the assumption that the heat capacity of acetylene is negligible, which seems reasonable although no experimental data are available, one has the free energy equation:

$$\Delta F = \Delta H + IT = 54{,}900 + IT$$

in which I is, of course, the integration constant. A value of -13.6 has been derived for it from equilibrium data for

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[1] **Parks and Huffman, *The Free Energies of Some Organic Compounds*. Reinhold, New York, 1932, pp. 84–86.**

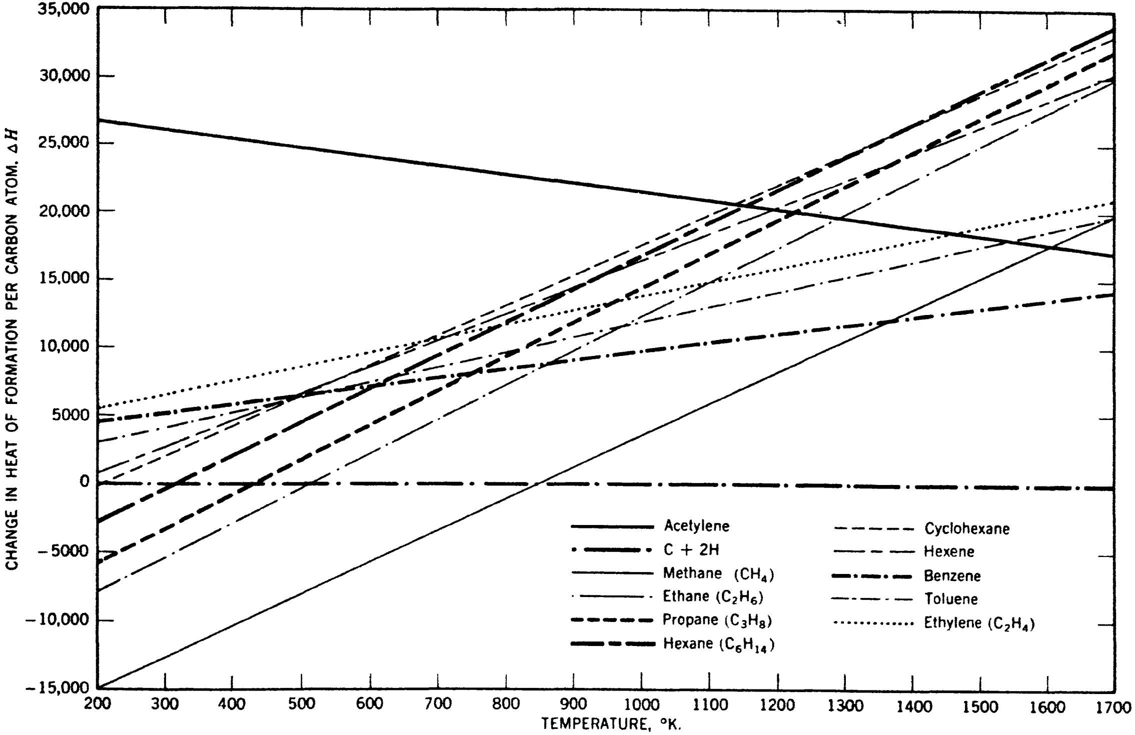

Fig. 1. Stability of representative hydrocarbons.

the formation of acetylene from carbon and hydrogen,[2] so that $\Delta F_{291} = 50{,}940$.

Another approximation, based on a reasonable assumption for the entropy of acetylene,[3] led to the figure 50,640.

If one plots the free energy, ΔF, of formation per carbon atom against the absolute temperature, one has the following picture[4] (see Fig. 1). If the horizontal line represents the system C + H_2, the paraffins are represented by a group of almost parallel straight lines. So are the olefins, which form a smaller angle against the C + 2 H line, and the aromatics, which are represented by still nearer horizontal lines.

All these hydrocarbons have higher free energies at higher than at lower temperature levels. The only exception is acetylene; its free energy decreases at higher temperatures. One can see that with increasing temperature there is a tendency for higher paraffins to form lower ones, for all paraffins to form olefins (ethane becomes less stable at 1090°K. than ethylene), and for the latter to form aromatics. Acetylene has the distinction that while it is less stable than ethylene at low temperatures, it becomes more stable at 1420°K. Indeed, at high temperatures it is more stable than any other hydrocarbon, but it must be borne in mind that, in turn, it is less stable than the free elements. These facts form the basis for the modern attempts to produce acetylene by high-temperature cracking of hydrocarbons, such as methane or natural gas. They require a temperature of not substantially less than 1200–1500°C., but one has to keep the contact time short to reduce the probability of the fall to the lowest level in the free energy diagram—that of the free elements. The two main methods which have been suggested and investigated in recent years as alternatives to the classical carbide process, thermal cracking, as most extensively studied in this country,[5] and the electric arc process, developed to large-scale performance in Germany,[6] show this feature. In the thermal process, using, *e.g.*, methane, one works with contact times of the order of magnitude of one tenth to one thousandth of a second—it is the longer, the lower the temperature used—and preferably in a partial vacuum as the reaction is accompanied by an increase in volume; the final gas volume, which contains 11% acetylene, is twice that of the charging stock at 1600°C. The reduction of the partial pressure can, of course, also be achieved by admixture of "inert" gases, such as hydrogen—in spite of the fact that the cracking leads to the formation of considerable quantities of that element.[6a] The presence of kaolin or similar substances appears advantageous.[7] As one would expect from the free energy diagram, higher paraffins give a better performance than methane. But even so, it does not seem possible to obtain an end gas with more than 15% of acetylene. The results obtained with the electric treatment appear to be superior. It would go too far to discuss here in detail the several devices by which the fundamental process has been improved in recent years, but let it be said that one can obtain 45 kg. of acetylene from 100 kg. of initial gas, and that one can suppress largely any side reactions apart from the formation of the valuable hydrogen.[8] The concentration of acetylene in the resulting gas mixture varies between 13 and 17%; its isolation is relatively simple.

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[2] von Wartenburg, *Z. anorg. Chem.*, 52, 299 (1907). Pring and co-workers, *J. Chem. Soc.*, 89, 1601 (1906); 97, 498 (1910); *Ind. Eng. Chem.*, 4, 812 (1912).

[3] Parks and Huffman, *loc. cit.* It is assumed that the entropy of acetylene is as much lower than that of ethylene as that of ethylene is lower than the entropy of ethane.

[4] See Parks and Huffman, *loc. cit.*, p. 99.

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[5] See Eymann, U. S. Pat. 1,957,254 (1934); *Chem. Zentr.*, **1936, I,** 1709. Wulff, U. S. Pat. 1,966,779 (1934); *Chem. Zentr.*, **1935, II,** 636. Dreyfus, Brit. Pat. 440,432 (1935); *Chem. Zentr.*, **1936, I,** 2795; Brit. Pat. 479,438 (1938); *Chem. Zentr.*, **1938, I,** 4379. Yamamoto, *J. Soc. Chem. Ind. Japan*, **38,** 550 (1935).

[6] Combined Intelligence Objectives Sub-committee, Item No. 22, File No. XXX-83 and File No. XXVI-51.

[6a] Fischer and Peters, German Pat. 641,091 (1937); *Chem. Zentr.*, **1937, I,** 3751. Fischer and Pichler, Brit. Pat. 416, 921 (1932); *Chem. Zentr.*, **1936, I,** 697. Bojko, *Khim. Tverdogo Topliva*, **7,** 59 (1936).

[7] Kubozeneg, *J. Gen. Chem. U.S.S.R.*, **5,** 134 (1935). Klyukiwin, *Khim. Tverdogo Topliva*, **6,** 130 (1935).

There are a number of selective solvents in existence, the most obvious of them being water, which under pressure absorbs considerable amounts of the gas and releases them when the pressure is lifted. A number of other selective solvents has been suggested: the classical acetone, tetramethylurea and *N*-dimethylformamide by duPont,[9] and glycol monoethyl ether (Cellosolve).[9a] Koller[10] has found for this solvent, which has a satisfactorily low vapor pressure, the following relative absorption coefficients: acetylene, 24,000; ethylene, 4100; ethane, 3700; methane, 460; H, 1.

In summarizing, it should be noted that the consumption of electric energy for each cubic meter of acetylene produced in the arc process does not appear to differ from the figure accepted for the classical carbide process, which is 1 to 1.35 kilowatt hours per 100 liters of acetylene. The arc process is said to require 1.16 to 1.28 kilowatt hours per 100 liters, 10 to 11 kilowatt hours per kg. (= 862 liters) of acetylene. It appears, therefore, that it is more the raw material availability than the cost which determines the type of process to be used in any particular instance. I would suggest that we do not go into details regarding the several modifications of these fundamental methods, such as the "incomplete combustion of methane," which employs, instead of external heating, the heat of combustion of part of the methane by injected oxygen to raise the gas to the temperature required for cracking. I would rather draw your attention to two points which appear interesting.

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[8] In addition to the acetylene, 100 kg. of starting material (mostly methane) gave 9.2 kg. of ethylene, 5.3 kg. of carbon black, and 142.5 m.^{3} of pure hydrogen. The hydrogen was isolated and used for the catalytic hydrogenation of acetylene to ethylene.

[9] Du Pont, U. S. Pat. 2,146,448 (1939); *Chem. Abstracts,* **33,** 3398 (1939).

[9a] Isham [U. S. Pat. 2,424,987 (1947); *Chem. Abstracts,* **41,** 6694 (1947)], has suggested the use of tetrahydrofuryl acetate for the isolation of acetylene.

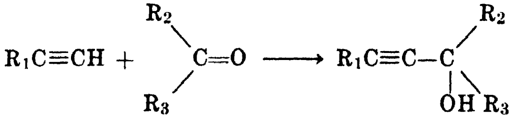
[10] Koller, *Khim. Tverdogo Topliva,* **8,** 1149 (1937); *Chem. Abstracts,* **32,** 4016 (1938).

Exactly the same situation, from a thermochemical and from a practical point of view, as in the manufacture of acetylene exists in the production of nitric acid from nitrogen and oxygen. Nitrogen like methane is a very inert gas, and the stable level of the system nitrogen–oxygen is that of the mixture of the elements. At high temperatures oxides are formed, but only if the time of contact is very low, can one avoid the reversion of the gas mixture to that lowest energy level. Recent processes developed in this field appear to be, indeed, an exact replica of the high-temperature conversion of methane into acetylene.

The second point I would like to mention is the fact that an interesting by-product of the arc process is diacetylene. It is removed by passing the crude gas through a solvent which dissolves diacetylene preferentially. Its formation is most likely due to a thermal dehydrogenation process leading to an ethinyl radical which dimerizes.[10a] We will in the course of our discussion meet similar cases, in which such a dehydrogenation is affected by chemical means. The investigation of the thermal behavior of acetylene had led to the conclusion that radicals are formed.[11] The kinetics, of course, does not show whether the radicals have the structure CH or C_2H, the former being unlikely for thermochemical reasons. In any event, the fact that the thermal dissociation is inhibited by nitric oxide shows that radicals are carriers of the reaction.[12] This reaction implies certain interesting possibilities. The loosening of hydrogen atoms linked to an unsaturated carbon atom is here carried to the extreme, *i.e.*, the rupture of the bond; it expresses itself also in other reactions of acetylenes which we will have to study, *e.g.*, the condensation with carbonyl compounds according to the scheme:

[10a] See Zelinski, *Ber.*, 57, 264 (1924). Schaepfer and Brunner, *Helv. Chim. Acta*, 13, 1125 (1930).

[11] See the discussion in Steacie, *Atomic and Free Radical Reactions*. Reinhold, New York, 1946, p. 164.



$$R_1C\equiv CH + \begin{matrix} R_2 \\ & \diagdown \\ & & C{=}O \\ & \diagup \\ R_3 \end{matrix} \longrightarrow R_1C\equiv C-\overset{\diagup R_2}{\underset{OH\ \diagdown R_3}{C}}$$

Similar reactions in the ethylene series are known. Asymmetric disubstituted ethylenes condense with formaldehyde to give substituted allyl alcohols, $R_2C{=}CHCH_2OH$[13]; they react with *N*-methylformanilide to give aldehydes, $R_2C{=}CHCHO$, with the elimination of methylaniline,[14] and couple with diazonium compounds to azo dyes; $R_2'C{=}CHN{=}NAr$.[15] It would, therefore, not be impossible, and it would certainly be interesting, to dehydrogenate ethylenes, too, in a bimolecular reaction which would lead from ethylenes to dienes, and from dienes to more highly unsaturated hydrocarbons. Such thermal reactions are known in the aromatic series: to them belong the classical transformations of benzene to biphenyl, of naphthalene to dinaphthyl, of 1,1′-dinaphthyl to perylene.[16]. They can be accelerated by catalysts which loosen the C—H bond as recently shown by Orchin[17] in a series of papers, and one might add that ultraviolet light, too, has this effect in a number of cases. The so-called dianthraquinone, *e.g.*, is dehydrogenated to a more closely condensed polycyclic ring system,[18] and a similar reaction is known for benzhydrylideneanthrone:[19]

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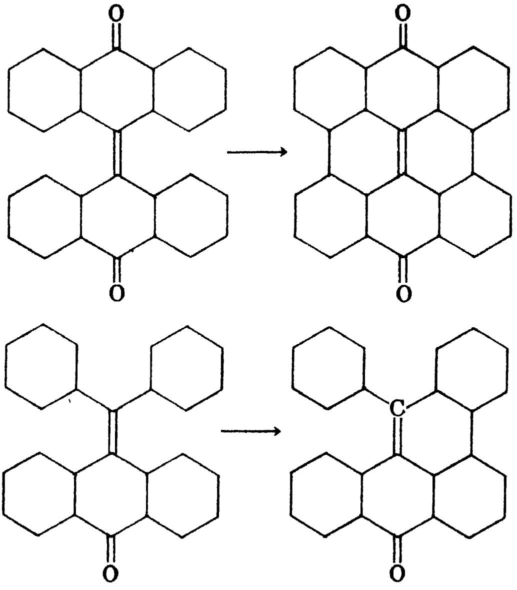
[12] Burnham and Pease, *J. Am. Chem. Soc.*, 64, 1404 (1942). Frank-Kamenetzky, *Acta Physicochim. U.S.S.R.*, 18, 148 (1943).

[13] See, for example, the reaction of β-pinene, Bain, *J. Am. Chem. Soc.*, 68, 638 (1946).

[14] Lorenz and Wizinger, *Helv. Chim. Acta*, 28, 600 (1945).

[15] Wizinger and Cyriax, *Helv. Chim. Acta*, 28, 1018 (1945).



But let us return from this digression to acetylene and try to relate that peculiar bimolecular dehydrogenation reaction of acetylene to its molecular structure. It is a completely symmetrical molecule of the form of a handlebar.[20] This follows both from the fact that acetylene and its dialkyl derivatives have no finite electric moment[21] and also from a study of the spectrum. The ultraviolet spectrum[22] is not as interesting as in the case of the olefins; the triple bond does not shift the absorption of the molecule to the visible as the double bond does. Indeed, from their ultraviolet spectra the acetylenes appear more saturated than the olefins, and in common usage the acetylenic group is not considered a chromophor. However, the ultraviolet spectrum gives us some information as to the relative strengths of the $C \equiv C$ and the C—H bonds. The energy required to split the $C \equiv C$ bond is 187 kcal. per mole; the energy required for the fission of the C—H is 121 kcal. per mole. We have here an indication as to why the thermal bimolecular dehydrogenation of acetylene is possible. The infrared[23] and the Raman spectra,[24] especially the polarization of the Raman lines, give us better information. In the infrared spectrum one has two active frequencies at 3.05 and 13.71, which must be attributed to the following two types of vibration:

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[16] In the presence of aluminum chloride. Scholl, Seer, and Weitzenboeck, *Ber.*, **43**, 2203 (1910).

[17] Orchin and co-workers, *J. Am. Chem. Soc.*, **67**, 122,499 (1945); **68**, 571, 573 (1946).

[18] H. Meyer, *Monatsh.*, **33**, 1465 (1912).

[19] Schoenberg, Ismail, and Asker, *J. Chem. Soc.*, **1946**, 492. See Clar, *Ber.*, **63**, 869 (1930).

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[20] For the x-ray analysis of acetylenedicarboxylic acid dihydrate, see Dunitz and Robertson, *J. Chem. Soc.*, **1947**, 148.

[21] Smyth and Zahn, *J. Am. Chem. Soc.*, **47**, 2505 (1925). Wenzke and co-workers, *ibid.*, **56**, 858, 2025 (1934); **57**, 668, 1265 (1935); **59**, 943, 2301 (1937). Watson, Rao, and Ramaswamy, *Proc. Roy. Soc. London*, **A143**, 558 (1939).

[22] Gordon, *J. Chem. Phys.*, **3**, 259 (1935). Price, *Phys. Rev.*, **45**, 483 (1934); **47**, 444 (1935). Cherton, *Bull. soc. chim. Belg.*, **52**, 26 (1943). See also page 20.

[23] Of the numerous papers the following may be cited: Sutherland, *Nature*, **134**, 775 (1934); *Phys. Rev.* [2], **43**, 883 (1933). Bradley and McKellar, *ibid.*, **46**, 664 (1934); **47**, 914 (1935). Mecke and co-workers, *Z. Elektrochem.*, **40**, 474 (1934); *Z. Physik*, **99**, 189 (1936); **101**, 405 (1936). Herzberg, Patat, and Spinks, *Nature*, **133**, 951 (1934).

[24] See, for example, Glockler and Davis, *J. Chem. Phys.*, **2**, 881 (1934); *Phys. Rev.*, **46**, 535 (1934). Wu and Kiang, *J. Chem. Phys.*, **7**, 178 (1939).

$$\begin{array}{cccc} H & {-}C\equiv & C{-} & H \\ \rightarrow & \leftarrow & \leftarrow & \rightarrow \\ \uparrow & \downarrow & \downarrow & \uparrow \end{array}$$

In the Raman spectrum, the other three vibrations are indicated, with varying intensity:

$$\begin{array}{ccccl} \rightarrow & \rightarrow & \leftarrow & \leftarrow & \quad \lambda = 5.06 \\ \rightarrow & \leftarrow & \rightarrow & \leftarrow & \quad \lambda = 2.97 \\ \downarrow & \uparrow & \downarrow & \uparrow & \quad \lambda = 16.6 \end{array}$$

The Raman spectrum permits the calculation of the interatomic distances, for which $C{-}H = 1.058$ and $C{\equiv}C = 1.199$ has been found by Herzberg and co-workers,[25] in satisfactory agreement with the values 1.058 and 1.205 which Pauling and his school[26] have derived from electron diffraction experiments. This appears to give a complete picture of the molecule, and it may be added that the same straight model has been arrived at in the classical stereochemical theory. The two carbon tetrahedra have one face in common, and the two other apices and the two carbon atoms lie, therefore, in one line. It is, however, difficult, to understand why such a molecule should appear from its spectrum to be more saturated than ethylene. Equally, the characteristic increment which is caused by the triple bond in the molecular magnetic susceptibility is low.[27] While its value for the double bond is 57×10^{-7}, it is 8×10^{-7} for the C_2H_2 system. The $C{\equiv}N$ triple bond too—we will return to this point presently—has an increment of 8 × 10^{-7}, whereas that of the C═N double bond is 85 × 10^{-7}. One might well see in these phenomena simply an expression of the high symmetry of the molecule. There may also be an influence of the specific character of the bonds. The length of the C—H bond (see above) indicates that it is different from the paraffinic, olefinic, and even aromatic C—H bonds, which difference expresses itself also in the energy required for bond fission. Another fact pointing in the same direction is the finite dipole moment of substances like phenylacetylene.[28] While styrene has no finite moment, phenylacetylene has $\mu = 0.83$. Equally, phenylchloroacetylene has a moment of 1.10, while ω-bromostyrene has 1.49. One could express this latter fact by saying that the chlorine is more positive in phenylchloroacetylene, or that a structure like $C_6H_5\overset{-}{C}{=}C{=}\overset{+}{Cl}$ contributes considerably to the actual state of the molecule. To this problem of the possible participation of the triple bond in resonance phenomena, we will have to return at a later occasion.

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[25] Herzberg, Patat, and Spinks, *Nature*, 133, 951 (1934); *Z. Physik*, 92, 87 (1934).

[26] Pauling, Springall, and Palmer, *J. Am. Chem. Soc.*, 61, 927 (1939).

[27] Pascal, *Compt. rend.*, 180, 1596 (1925); *Bull. soc. chim.*, 11, 636 (1912).

In any event, these peculiarities of the C—H bond will make understandable the very characteristic reactions of which acetylene and its derivatives are capable. Let us first consider halogenation. The normal addition leads to a dihalogenoethylene and further to a tetrahalogenoethane; only iodine is not capable of forming tetraiodoethane. Substituents influence considerably the character of this reaction. Tolane can give a tetrachloro, but only a dibromo and diiodo derivative,[29] and α,β-acetylenic acids generally give only dihalogeno addition products.[30] A very curious reaction which recalls the high-temperature formation of diacetylene takes place when acetylene is treated at high temperatures with an excess of chlorine. This reaction leads into hexachlorobutadiene.[31] Similar phenomena have been observed in the photobromination of acetylene, which was studied extensively by Schumacher and his co-workers.[32] It is a reaction of bromine atoms, which leads to an intermediate radical with the structure $\underset{:}{C}H{=}CHBr$. This can either dissociate or react with a bromine molecule according to the scheme $\underset{:}{C}H{=}CHBr + Br_2 \rightarrow CHBr{=}CHBr + Br$. Both secondary reactions are, therefore, carriers of the chain reaction, which makes it understandable that the photobromination of acetylene has a very high quantum yield: 10^4 molecules per quantum absorbed. A similar chain reaction must be assumed to explain the formation of a flame when acetylene and chlorine are mixed;[33] the carrier of this thermal chain would be $\underset{:}{C}H{=}CHCl$. Of course, the mechanism of chemical bromination is different; it can best be understood on the basis of the hypothesis that on the whole the carrier of the reaction is a negative bromide ion.[34] This explains, indeed, that the bulk of the dihalogen addition products frequently have *trans* structures, as evidenced by their dipole moments.[35] The presence of a bromine atom will always direct the next one—for electrostatic reasons—to a place most remote in the molecule. The minor quantities of *cis*-dihalogenoethylenes may owe their formation to a previous association between the triple bond and a halogen *molecule.*

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[28] Pflaum and Wenzke, *J. Am. Chem. Soc.*, 56, 1106 (1934). Otto and Wenzke, *ibid.*, 56, 1314 (1934). Wilson and Wenzke, *ibid.*, 56, 2025 (1934).

[29] Beilstein, Vol. V, p. 656. E. Fischer, *Ann.*, 211, 233 (1882). For the addition of dithiocyanogen, see Soederbaeck, *ibid.*, 443, 147, 161 (1925). Bried and Hennion, *J. Am. Chem. Soc.*, 60, 1719 (1938).

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[30] See, for example, Bandrowsky, *Ber.*, **12**, 2213 (1879).

[31] French Pat. 875,382 (1942).

[32] Franke and Schumacher, *Z. physik. Chem.*, **B34**, 181 (1936). Mueller and Schumacher, *ibid.*, **39**, 352 (1938); **40**, 318 (1938).

[33] Tominaga and Okamoto, *Bull. Soc. Chem. Japan*, **12**, 401 (1937). Steacie, *Atomic and Free Radical Reactions.* Reinhold, New York, 1946, p. 415.

[34] See E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937).

[35] See E. Bergmann and A. Weizmann, *Chem. Revs.*, **29**, 553 (1941).

This explanation is in keeping with the observations made in the hydrogenation of acetylenic bonds. While the final product of such reactions is the paraffinic derivative, it is possible to stop the reaction at the ethylene stage. This is the case for the chemical reduction with the copper-zinc couple,[36] for the electrochemical reduction,[37] and also for some catalysts in the catalytic hydrogenation.[38] The situation, however, in the case of catalytic hydrogenation, is very much less clear than the literature leads one to expect; evidently a number of factors play an uncertain and undetermined role. It has, for example, been found[39] that 1-ethynylcyclohexanol can be hydrogenated to the vinyl compound in the presence of palladium–barium sulfate only when the catalyst was previously heated at 600–700°.

The mechanism of such a catalytic hydrogenation explains why the product contains the entering hydrogen atoms in *cis* position.[40] The reaction takes place in the adsorbed phase, and undoubtedly the acetylene molecule is adsorbed so its active points, at which the equally adsorbed hydrogen enters, are in immediate vicinity to each other.

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[36] See, for example, Straus, *Ann.*, **342**, 201 (1905).

[37] See, for example, Favorski, *Chem. Zentr.*, **1936**, I, 1709; Azerbow, *Chem. Abstracts*, **40**, 4683 (1946).

[38] Nickel (for disubstituted acetylenes only): Kenneth, Campbell, and Connor, *J. Am. Chem. Soc.*, **61**, 2897 (1939). Active iron: Paul and Hilly, *Compt. rend.*, **206**, 608 (1938); *Bull. soc. chim.*, **6**, 218 (1939). Platinum and palladium: Paal and co-workers, *Ber.*, **48**, 277, 1195, 1202 (1915). Bourguel, *Bull. Soc. Chim.*, **41**, 1443 (1927). Zalkind and co-workers, *Chem. Zentr.*, **1933**, I, 2541; **1933**, I, 2587; **1939**, II, 2422.

[39] Gibson, *J. Chem. Soc.*, **1945**, 713; and unpublished results from our laboratories.

[40] See A. and L. Farkas, *Trans. Faraday Soc.*, **33**, 837 (1937).

The *addition* of halogen is not the only reaction of which acetylene and its derivatives are capable. In alkaline solution, halogen, *i.e.*, hypohalogenite, does not add as it does to the double bond. It substitutes terminal hydrogen atoms.[41] The analogous diiodination can also be carried out by iodine in liquid ammonia.[42] One may well assume that this is a reaction of the acetylene ion, which would mean that the hydrogen of the acetylene is capable of ionization, that the process is intensified by the alkaline medium, and that acetylene is a pseudo acid (of which one can, at least formally, define the dissociation constant).[43] This approach gives us an explanation of many properties of the acetylene derivatives some of which we have already discussed. An interesting example is to be seen in the observation that acetylene can undergo a reaction with dialkylamines and formaldehyde in complete analogy to the Mannich reaction of ketones, in which a hydrogen atom is activated by the immediately adjacent carbonyl double bond.[44]

$$\mathrm{RCOCH_3} \longrightarrow \mathrm{RCOCH_2CH_2NR_2}$$

C_2H_2 gives $R_2NCH_2C{\equiv}CH$ and $R_2NCH_2C{\equiv}CCH_2NR_2$, a reaction which applies equally to all acetylenic compounds possessing a terminal hydrogen atom.

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[41] Straus, Kollek, and Heyn, *Ber.*, 63, 1868 (1930). Straus, Kollek, and Hauptmann, *ibid.*, 63, 1886 (1930). Dehn, *J. Am. Chem. Soc.*, 33, 1598 (1911).

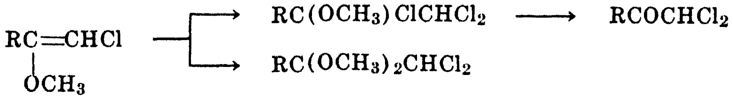
[42] Vaughn and Nieuwland, *J. Am. Chem. Soc.*, 54, 787 (1932).

[43] For measurements of the "acidity" of hydrocarbons, see: Conant and Wheland, *J. Am. Chem. Soc.*, 54, 1212 (1934); McEwen, *ibid.*, 58, 1124 (1936).

[44] In the case of acetylene itself, copper acetylide (see page 6) is necessary as catalyst: French Pat. 859,875 (1940). Arylacetylenes react more easily: Mannich and Chang, *Ber.* 65, 418 (1933); so does vinylacetylene: Coffman, *J. Am. Chem. Soc.*, 57, 1978 (1935). See Carothers, U. S. Pat. 2,110,199 (1938); *Chem. Abstracts*, 32, 3418 (1938).

The halogen-substituted acetylenes become, in contact with oxygen, highly explosive; indeed, they have occasionally been suggested as material for high-explosive bombs.

It is interesting that a variation in the procedure permits the "normal" hypochlorous acid reaction of the triple bond. If one uses the system methanol–chlorine (instead of aqueous alkali and chlorine), one observes the following series of reactions:[45]



$$\underset{\displaystyle OCH_3}{RC}{=}CHCl \longrightarrow \begin{cases} RC(OCH_3)ClCHCl_2 \longrightarrow RCOCHCl_2 \\ RC(OCH_3)_2CHCl_2 \end{cases}$$

It might be worth our while to interrupt the logical pursuit of the subject and to discuss a problem which has interested the workers in this field for quite a time. Certain reactions of the mono- and dihalogenated acetylenes have been explained occasionally by the assumption, first propounded by Nef,[46] that they are capable of forming isoacetylenic structures with divalent C, derived from a hypothetical isoacetylene: $CH_2{=}C\colon$. As an argument the fact was used that the analogous hydrocyanic acid can react in two forms, the nitrile and the isonitrile forms, which appear stable in their alkyl derivatives. In order to explain that the interaction of monochloroacetylene with hypobromous acid leads both to chloroacetyl bromide and chlorodibromoacetaldehyde, two parallel mechanisms have been assumed:

$$CCl{\equiv}CH \longrightarrow CClBr{=}CHOH \longrightarrow CHClBrCHO \longrightarrow CClBr_2CHO$$

$$CHCl{=}C\colon \longrightarrow CHCl{\equiv}CBrOH \longrightarrow CH_2ClCOBr$$

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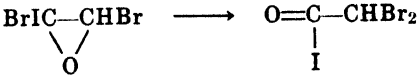
[45] Hennion and co-workers, *J. Am. Chem. Soc.*, **60**, 1711 (1938); **62**, 449 (1940).

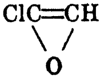
[46] Nef, *Ann.*, **298**, 332 (1897); **308**, 264 (1899). Lawrie, *Am. J.*, **36**, 487 (1906).

Equally, the reaction of dibromoacetylene with hydriodic acid leads to a dibromoiodoethylene which upon oxidation gives dibromoacetic acid and should be $CBr_2 = CHI$ (which is derived from $Br_2C = C\colon$) and not $CBrI = CHBr$ (derived from $BrC{\equiv}CBr$) etc. Now, one knows from physical evidence that the dihalogenoacetylenes are symmetrical: the molecule of the dichloro compound is linear, the C—C distance being 1.195 Å, the C—Cl distance, 1.64 Å.[47] The same follows from the Raman spectrum of diiodoacetylene.[48] Furthermore, chloroacetylene was known to trimerize to 1,3,5-trichlorobenzene.[49] One has to assume[50] that the —obviously—abnormal reactions are due to intramolecular rearrangements. C_2Br_2 and HI, for example, actually give $CBrI{=}CHBr$, but the oxidation proceeds via a glycol or an ethylene oxide (thus a system capable of, at least formally, a pinacolinic rearrangement) which can rearrange in the following way:



$$\underset{\diagdown\ \diagup \atop O}{BrIC{-}CHBr} \longrightarrow O{=}\underset{\mid \atop I}{C}{-}CHBr_2$$

Equally, monochloroacetylene and hypobromous acid give only:



$$\underset{\diagdown\ \diagup \atop O}{ClC{=}CH}$$

which is able to add either hydrogen bromide or free bromine as shown in scheme (I).

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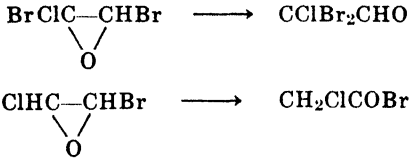
[47] Hassel and Taarland, *Chem. Zentr.*, 1942, II, 878.

[48] Glockler and Morrel, *J. Chem. Phys.*, 2, 349 (1934).

[49] Ingold, *J. Chem. Soc.*, 125, 1536 (1924).

[50] See Biltz, *Ber.*, 46, 143 (1913).

These reactions would be fully in accordance with the old observation that in the oxidation of halogenated ethylenes (where no doubt exists as to their molecular structure), rather complicated rearrangements also exist. *Asym.* dibromoethylene gives monobromoacetyl bromide,[51] 1-chloro-1-bromoethylene gives both chloroacetyl bromide and bromoacetyl chloride,[52] and tetrabromoethylene gives tribromoacetic acid.[53] Indeed, under conditions when isoacetylenic compounds could be formed, migratory symmetrization takes place. When, *e.g.*, *asym.* diphenyldibromoethylene is treated with alkali metals, the same products are obtained as if tolane is treated with these metals.[54]



(I)

On the whole, therefore, the addition reactions of acetylene are similar, if perhaps more vigorous, than those of the corresponding olefinic compound. However, acetylenes are capable of further reactions, which are either not known for, or less readily undergone by, ethylene derivatives. The best known is the hydration, which converts acetylene into acetaldehyde,[54a] monosubstituted acetylenes into ketones.

[51] Swarts, *Bull. Acad. Roy. Belg.*, **34**, 317 (1897); **35**, 849 (1898); **36**, 540 (1898).

[52] Demole, *Ber.*, **11**, 1303 (1878).

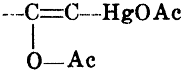
[53] Nef, *Ann.*, **308**, 324 (1899).

[54] Schlenk and E. Bergmann, *Ann.*, **463**, 81 (1928).

[54a] Compare the recent paper by Yakubowich *et al.*, *Chem. Abstracts*, 41, 4367 (1947); also Mita, *ibid.*, 41, 3038 (1947).

From disubstituted acetylenes also, ketones are formed, and if one tries to formulate a general rule for unequally disubstituted acetylenes, one might say that both possibilities are equally favored, *e.g.*, from 9,10-undecynoic acid, 46% of the 9- and 51% of the 10-keto compound are obtained under the standard conditions (acid in the presence of a mercuric salt).[55] However, when α,β-acetylene ketones are hydrated, the new keto group always occupies the β-position with relation to the one already present in the molecule.[56]

It is very probable that the intermediate step is the formation of an enol or rather that the mercuric salt $(AcO)_2Hg$ forms an addition product:



$$\begin{array}{l}\text{—C}{=}\text{C—HgOAc}\\ \;\;\,| \\ \;\;\text{O—Ac}\end{array}$$

which contains the system of the enol, liberated by hydrolysis. Indeed, one often observes in these hydration reactions the transient formation of a complex mercuric compound. The occurrence of a C—Hg bond might well be the point at which a frequently encountered side reaction sets in, *viz.*, the reduction of the mercuric to the mercurous stage or to metallic mercury. This one tries to counteract, at least in the large-scale production of acetaldehyde, by adding to the solution certain oxides which can reoxidize the mercurous to the mercuric salt, *e.g.*, ferric or manganese oxide (MnO_2). There are cases in which mercuric salts are not necessary, *i.e.*, those in which the triple bond is in the immediate vicinity of a phenyl, carbonyl, or carboxyl group. In these cases, concentrated sulfuric acid alone causes the formation of a ketone.[57]

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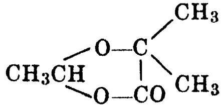
[55] Sherill and Smith, *J. Chem. Soc.*, 1937, 1501.

[56] Moureu and Delange, *Compt. rend.*, 131, 710 (1900). Nef, *Ann.*, 308, 277 (1899).

[57] A. von Baeyer, *Ber.*, 15, 2705 (1882); 16, 2128 (1883). Tolane is hydrated to desoxybenzoin with water alone at an elevated temperature; Desgrez, *Ann. chim. phys.*, 3, 209 (1894).

A good argument in favor of the intermediate enol formation is the fact[58] that, in the presence of alumina at 400–425°C, acetylene reacts with water to give furan (and hydrogen); an even better argument is based on a reaction which is hardly known in the ethylene series, the addition of alcohols to acetylene, which leads to vinyl ethers,[59] although the reaction need not stop at this stage but can lead, by addition of a second molecule of the alcohol, to acetals.[60] Here, too, mercuric salts are the catalysts of choice in acid medium; however, boron trifluoride in conjunction with acetic acid is also suitable. The regularities of addition are the same as for the hydration process. Not only alcohols, but also glycols undergo this reaction; propylene glycol, for example, gives the cyclic acetal of acetaldehyde (2,4-dimethyldioxolane),[61] mannitol gives a tricyclic hexaacetal,[62] and it is interesting that α-hydroxyisobutyric acid gives an acetal-like compound of the formula:[62a]



This latter reaction indicates that acids, too, can react with acetylenes. Indeed, not only the normal addition of hydrochloric acid and its inorganic analogs is possible, leading to vinyl halides[62b] and further on to dihalogenoethanes —organic acids, too, fix themselves under the influence of the same type of catalysts; this, indeed, represents a practical method for the manufacture of vinyl acetate.[62c] Another important example is the production of vinyl methacrylate which, copolymerized with methyl methacrylate, has given an interesting plastic, interesting especially from the optical point of view. The vinyl group, not participating in the chain formation, increases the refractive index of the material.

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[58] Tchitchibabin, *Chem. Zentr.*, 1916, I, 920.

[59] Griesheim Elektron, Brit. Pat. 14,246 (1913); German Pat. 271,381 (1915); French Pat. 461,223 (1913). Klatte, U. S. Pat. 1,084,581 (1914). Boiteau, Brit. Pats. 15,806 and 15,919 (1914). Plauson, Brit. Pat. 156,121 (1920); U. S. Pat. 1,436,388 (1923).

[60] Reichert, Bailey, and Nieuwland, *J. Am. Chem. Soc.*, 45, 1552 (1923). Hill and Hibbert, *ibid.*, 45, 3108 (1923). Nieuwland and co-workers, *ibid.*, 52, 1018, 2892 (1930); 53, 3835 (1931); 56, 1130, 1384, 1786 (1934); 51, 2006 (1935); 58, 80, 892, 1658 (1936).

[61] Hill and Hibbert, *J. Am. Chem. Soc.*, 45, 3108 (1923).

[62] Killian, Hennion, and Nieuwland, *J. Am. Chem. Soc.*, 58, 1658 (1936).

[62a] See Stanley, Brit. Pat. 575,381 (1946); *Chem. Abstracts*, 41, 5544 (1947). V. Conaway, U. S. Pat. 2,270,779 (1945); *Chem. Abstracts*, 40, 367 (1946).

This whole field of chemistry has been put on a new basis by the research which before and during the war was carried out in Germany and which is linked with the name of Reppe.[63] In contradistinction to the classical type of catalyst, it was found that alkaline compounds catalyze the same reactions in vapor phase and permit the addition of many other reagents, all leading to vinyl compounds, so that "vinylation" has become an operation as important and almost as easy as nitration or sulfonation. Seemingly, however, the method has a drawback: it requires working with acetylene under pressure. But a thorough study has shown that the hazard of this work is much less than the prejudice of the organic chemist would have permitted him to believe. In the presence of an alkali alkoxide or hydroxide or strongly alkaline-reacting salts such as potassium or sodium cyanide, acetylene reacts with alcohols at a temperature of 150–160° to give the corresponding vinyl ethers in excellent yield. For alcohols boiling near or below this temperature, pressure is required. In some special cases, zinc or cadmium salts of organic acids need be used as catalysts,[64] bringing the reaction back to the old mercuric salt system.

[62b] Freed, U. S. Pat. 2,411,962 (1946); *Chem. Abstracts*, 41, 2072 (1947). Distillers Co., Brit. Pat. 578,405 (1946); *Chem. Abstracts*, 41, 2072 (1947). For the preparation of vinyl fluorides, see du Pont, Brit. Pat. 580,910 (1946); *C. A.*, 41, 2428 (1947).

[62c] Of recent processes, see I.C.I., Brit. Pat. 581,501; *Chem. Abstracts*, 41, 2428 (1947).

[63] Reppe, *Advances in Acetylene Chemistry*. Technical Report from Reconstruction Finance Corporation, Office of Rubber Reserve, Research and Development Section, July 25, 1945.

All aliphatic and hydroaromatic alcohols, diols, and polyols react equally well. Glycols can give mono- or divinyl ethers or cyclic acetals, according to conditions. Only tertiary alcohols are characterized by a relatively low rate of reaction. Phenols are also vinylated analogously. The vinyl ethers readily add a second molecule of a hydroxyl compound to give the corresponding acetals.[64a] This reaction takes place if one merely heats the components; it is accelerated by traces of hydrogen halides or of boron trifluoride.[65] As these vinyl ethers decompose easily in the presence of dilute acids into the corresponding alcohol and acetaldehyde, one has here a method of producing the latter which does not require mercuric salts. In our next seminar we will see that the fundamental reaction is probably one of potassium acetylide,[66] and that another set of analogous reactions involving this compound has been developed independently.

The zinc or cadmium salts which we mentioned as occasional catalysts for the vinylation of alcohols permit a number of other reactions which we might usefully mention in order to round off the picture. Phenols are not *O*-vinylated in their presence (in the gas phase), but the vinyl group enters the nucleus,[67] to give *o*- and *p*-vinylphenols, possibly

[64] I. G. Farbenindustrie, Brit. Pat. 430,590 (1935); German Pat. 643,270 (1937). Reppe and Wolff, U. S. Pat. 2,017,355 (1935).

[64a] Shostakovskii and Gershtein, *Chem. Abstracts*, 41, 1999 (1947).

[65] Cleavage of acetals to vinyl ethers in the presence of silver, gold, or platinum metals: I. G. Farbenindustrie, Brit. Pat. 345,253 (1929); German Pat. 525,836 (1931); French Pat. 703,509. (1931). Baur, U. S. Pat. 1,931,858 (1934).

[66] Favorski [*Chem. Zentr.*, 1887, 1539; *J. prakt. Chem.*, **37**, 382 (1889); **44**, 208 (1891)] assumed that alkali alcoholates add to the triple bond of acetylenic hydrocarbons.

[67] I. G. Farbenindustrie, Brit. Pat. 413,640 (1934); *Chem. Zentr.*, **1937**, II, 4421.

by an intramolecular rearrangement of a vinyl ether primarily formed, similar to the Claisen and the Fries rearrangements of phenol ethers and phenol esters, respectively. The reaction products polymerize spontaneously. The same catalysts permit (in the liquid phase, for the lower acids under pressure, at 180°C.) the fixation of acids on the triple bond. Again, the yields are about 90%.

In exactly the same manner as the alcohols, their sulfur isologs can be vinylated; even hydrogen sulfide adds at about 200°C. in the presence of sodium hydrosulfide as catalyst (dissolved in polyglycol), but in this case the vinyl mercaptan is reduced by the excess of the hydrogen sulfide to ethyl mercaptan and this is partly vinylated to its vinyl ether.[68] More important, undoubtedly, is the possibility of vinylating amines in the presence of alkali, zinc or cadmium oxides, or their salts with organic acids, under pressure. Vinylation of secondary and primary aliphatic amines is an extremely complex reaction, as we will see presently, but in a number of well-defined cases it is possible to isolate the primary *N*-vinyl compounds, so that evidently the complexity of the reaction in other instances is due to the high reactivity of these primary condensation products. Pyrrole, indole, and carbazole, for example, as well as imidazoles and diarylamines—such as diphenylamine and the phenylnaphthylamines—are simply *N*-vinylated,[69] and *N*-vinylcarbazole has become of some importance in the high-polymer industry. The reaction is carried out at 180° under high pressure, preferably in an inert solvent such as hexahydroxylene. It might be added that the hydrohalides of tertiary amines also react with acetylene under pressure, even at a low temperature. They give trialkylvinylammonium halides, trimethylamine, e.g., neurine, and this reaction takes place without the help of any catalyst.

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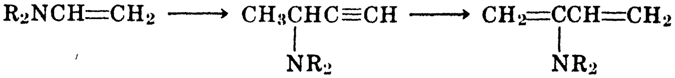
[68] Reppe and Nicolai, German Pats. 617,543 (1935), 625,660 (1936); *Chem. Zentr.*, 1936, I, 3908.

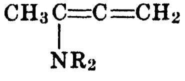
[69] Reppe, *Advances in Acetylene Chemistry, loc. cit.*

The understanding of the reactions which occur with aliphatic primary and secondary amines was made possible by a further development in general technique, *viz.*, the safe use of heavy-metal acetylides as catalysts under pressure. This appears to be still more hazardous than the use of acetylene under high pressure, but again the explosion limits of these systems have been carefully studied, although I still feel a certain awe even in reading the reports on this method and its manifold applications. In the presence of these catalysts, secondary amines react successively with two molecules of acetylene. The transient dialkylvinylamine reacts further to give a 3-substituted 1-butyne. An interesting, but not uncommon prototropic rearrangement of these 3-substituted 1-butynes leads to substituted 2-aminobutadienes:



$$R_2NCH{=}CH_2 \longrightarrow CH_3\underset{\underset{NR_2}{|}}{C}HC{\equiv}CH \longrightarrow CH_2{=}\underset{\underset{NR_2}{|}}{C}CH{=}CH_2$$

One has to assume, actually, a double prototropic shift, as undoubtedly the migration of the activated hydrogen atom leads in the first instance to an allene of the formula:



$$CH_3\underset{\underset{NR_2}{|}}{C}{=}C{=}CH_2$$

It is certainly time that we discuss a bit more thoroughly the metal derivatives of acetylene, the alkali acetylides and the heavy metal acetylides, which we have mentioned in the discussion. Before we do that, however, I suggest that we complete the picture of the reactions of the acetylene system by describing a wholly different type of addition reaction, which we might usefully relate to the hypothesis made before that the *cis* addition of halogen proceeds by a mechanism in which the molecules as such attract each other. The reaction to which I refer is that between acetylene and carbon monoxide.[70] Here, too, we have, in the activated form of the latter, two free valencies which can attach themselves to the two carbon atoms of the triple bond and give a cyclopropenone, of which one will expect a high degree of instability, since it is known that even the unsaturated four-membered cyclobutadiene is not stable, but isomerizes whenever its formation is expected. Indeed, for such a reaction, it will first be necessary to convert the carbon monoxide, which, as you know, is completely saturated, into a divalent radical. This appears to be possible by using nickel carbonyl or the system nickel salt plus carbon monoxide under conditions under which it tends to form the carbonyl, *i.e.*, at high temperatures and under high pressure. If one does that, acetylene reacts with carbon monoxide, and if water is present, the three-membered ring opens to give acrylic acid in quantitative yield; other substances with active hydrogen lead to derivatives of this acid, alcohols to its esters, amines to its amides. Two methods of procedure are, obviously, possible: one can use equimolecular amounts of nickel carbonyl, or employ as a catalyst the nickel salts which form the carbonyl and re-form when the latter reacts with the hydrocarbon. In the former case, one has to add an acid, *e.g.*, hydrochloric acid, as acceptor and one obtains as a by-product hydrogen, which under certain conditions, for example in glacial acetic acid as reaction medium, hydrogenates part of the acrylic to propionic acid. But the use of nickel carbonyl has the advantage that no pressure is required. This most elegant method, which is applicable to all acetylenic compounds, is limited to nickel as catalyst. Iron does not work, but it does not appear clear whether all iron carbonyls have actually been tested and found inoperative. In the case of substituted acetylenes both possible acids are normally obtained, *e.g.*, from phenylmethylacetylene, α-phenylcrotonic and β-methylcinnamic acids; from phenylacetylene, however, only α-phenylacrylic acid has been isolated. The occurrence of both acids is perhaps the best proof that a cyclopropenone is indeed the intermediate product.

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[70] *Recent Advances in the Chemistry of Carbon Monoxide.* British Intelligence Objectives Sub-committee, Final Report No. 355, Item No. 22.

From a more general point of view it is interesting to recall that both carbon monoxide and acetylene (in the form of calcium carbide) are formed in the same fundamental technical reaction, *viz.*, that between calcium oxide and carbon:

$$CaO + 3\ C \longrightarrow CO + CaC_2$$

It is equally of interest that olefins give the same reaction with carbon monoxide, but under much more extreme conditions, *i.e.*, at 200–300° and 150–300 atmospheres pressure. $RCH{=}CH_2$ thus gives a mixture of RCH_2CH_2COOH and $RCH(CH_3)COOH$, indicating that the first step of the reaction is the formation of a symmetrical intermediate, a substituted cyclopropanone.

The discussion of this reaction raises an interesting question: it has been known for some time[71] that under the catalytic influence of cuprous chloride and ammonium chloride in aqueous solution, acetylene reacts with hydrocyanic acid to give acrylonitrile. Of course, this might just be another addition of an acid to the triple bond, but it appears to me that the character of the catalyst employed casts some doubt on that mechanism. Would it not be possible that the hydrocyanic acid acts in its *iso* form and gives a cyclopropenone-imine which is then isomerized?

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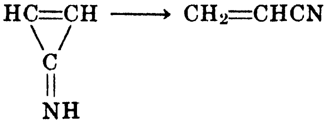
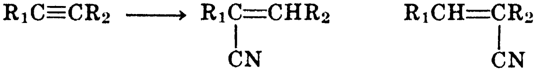
[71] See, for example, Kern and Fernow, *J. prakt. Chem.*, **160**, 281 (1942); Farlow and Lazier, U. S. Pat. 2,417,068 (1947); *Chem. Abstracts*, **41**, 3812 (1947); Hawk, U. S. Pat. 2,423,318 (1947); *Chem. Abstracts*, **41**, 6576 (1947). Compare also Consortium für elektrochemische Industrie A. G., German Pat. 559,734 (1930); *Chem. Zentr.*, **1932, II**, 3305—barium cyanide as catalyst. Francesconi and Ciuolo, *Gazz. chim. ital.*, **53**, 327 (1923)—silent electric discharge; formation of succinonitrile. Campbell, U. S. Pat. 2,415,441 (1947); *Chem. Abstracts*, **41**, 2747 (1947)—magnesium and cadmium oxides at below 380°; formation of succinonitrile. Owen and Kimberlin, U. S. Pat. 2,414,762 (1947); *Chem. Abtsracts*, **41**, 5894 (1947). Green and Taylor, U. S. Pat. 2,413,496 (1946); *Chem. Abstracts*, **41**, 1697 (1947). Harris, U. S. Pat. 2,413,623 (1946); *Chem. Abstracts*, **41**, 1697 (1947). Du Pont, Brit. Pat. 580,035 (1946); *Chem. Abstracts*, **41**, 2431 (1947).

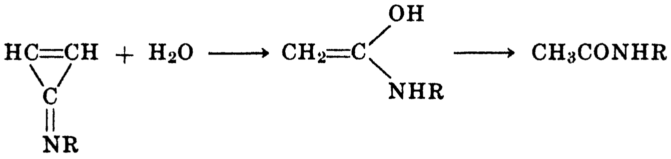


One might be able to verify this hypothesis by carrying out two experiments. The application of the method to a mono-substituted or unequally disubstituted acetylene should lead to a mixture of two different nitriles:



$$R_1C{\equiv}CR_2 \longrightarrow R_1\underset{\substack{|\\ CN}}{C}{=}CHR_2 \qquad R_1CH{=}\underset{\substack{|\\ CN}}{C}R_2$$

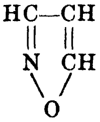
whereas the ordinary addition to the triple bond may be expected to give only one isomeride. Furthermore, isonitriles should behave in an analogous fashion, represented by the following sequence of reactions:



In this connection the recent observation may be of interest that over a zinc oxide catalyst at 425°, methylacetylene combines with hydrocyanic acid to give a mixture of the following substances indicating addition in both possible directions: 50-55% methacrylonitrile, $CH_2{=}C(CH_3)CN$; 25%

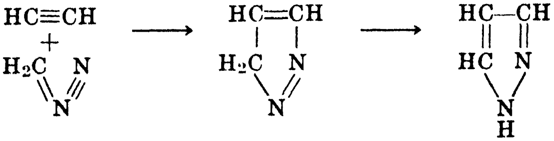
cis- and 15% *trans*-crotononitrile, $CH_3CH{=}CHCN$; and some allyl cyanide, $CH_2{=}CHCH_2CN$.[71a]

I should like to recall a very old reaction of acetylene, which belongs in this group, that with fulminic acid, considered as the oxime of carbon monoxide.[72] It reacted in a rather unexpected manner, leading to oxazole:



As the reaction was carried out in acetonic solution, the solvent condensed with the reactive hydrogen atom and gave (α-hydroxyisopropyl)-oxazole and its dehydration product.

There are a fair number of (in principle) similar reactions which we ought to discuss at this juncture. Diazomethane can be considered as a substance with two free valencies in the 1- and 3-positions; it is thus not surprising that it adds to triple bonds, forming pyrazoles:[73]



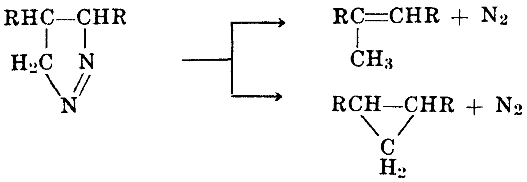
All diazo compounds, such as ethyl diazoacetate,[74] react in this way, and it is interesting to recall that the reaction has an analogon in the olefinic series, in which, however, the primary pyrazoline ring is not stable and loses nitrogen, forming a cyclopropane or a methylated olefin system:[75]

[71a] Butterbaugh and Spence, *Chem. Abstracts*, 41, 773 (1947); U. S. Pat. 2,407,472.

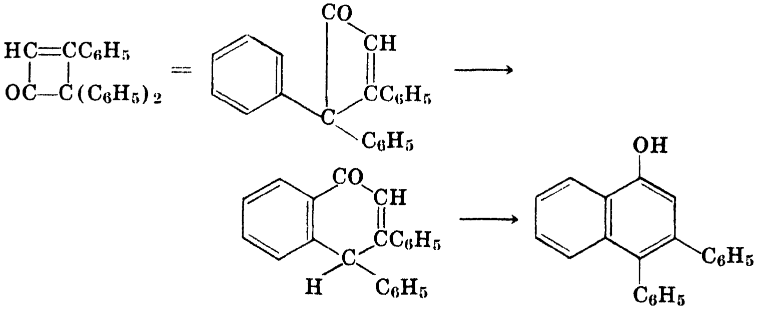
[72] Quilico and Speroni, quoted by Piganiol, *Acétylène, Homologues et Dérivés*. Masson, Paris, 1945, p. 215.

[73] Pechmann, *Ber.*, 31, 2950 (1898). Kuhn and Henkel, *Ann.*, 549, 219 (1941).

[74] Büchner, *Ann.*, 273, 252 (1893).



Diphenylketene has a similarly built unsaturated system (1,3); but it appears to react with phenylacetylene in a different manner, which involves the C=C double bond only. The final product has been identified as 3,4-diphenyl-1-naphthol[76] and I believe that this reaction proceeds in the following manner.[77] A four-membered ring is formed (in analogy to the behavior of olefins toward ketenes), which isomerizes by transfer of the hydrogen atom from the ortho position of one of the benzene nuclei:



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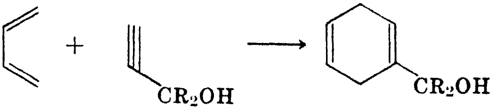
[75] von Auwers and Koenig, *Ann.*, 496, 252 (1932). von Auwers and Ungemach, *Ber.*, 66, 1198 (1933). E. Bergmann and F. Bergmann, *J. Org. Chem.*, 3, 125 (1938).

[76] Smith and Hoehn, *J. Am. Chem. Soc.*, 61, 2619 (1939).

[77] This mechanism differs slightly from that proposed by Smith and Hoehn, *J. Am. Chem. Soc.*, 63, 1181 (1941).

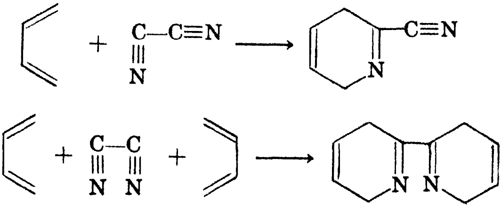
In favor of this explanation, the observation can be cited[78] that diphenylacetylene reacts analogously to give 2,3,4-triphenyl-1-naphthol so that the hydrogen atom appearing in the hydroxyl group could not be that originally present in the phenylacetylene molecule.

This reaction of a C=C double bond with the triple bond of an acetylene derivative raises the question whether acetylenes can function as dienophiles, so that the 1,4 valencies of the diene system attach themselves to the triple bond. No observations of this kind were known until recently when it was shown that acetylenic alcohols add to diene hydrocarbons to give alcohols of the dihydrobenzene series:[79]



Here a wide field for further research opens itself, which we are actively studying at present.

A parallel has recently been discovered[80] in the reaction between butadiene and cyanogen, which takes place at high temperatures and leads to α-cyanopyridine and α,α′-dipyridyl:



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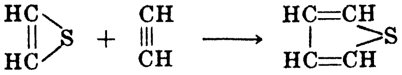
[78] Smith and Hoehn, *J. Am. Chem. Soc.*, **63**, 1180 (1941).

[79] British Intelligence Objectives Sub-committee, Final Report No. 266, Item No. 22, p. 15. Alder and Windemuth, U. S. Pat. 2,352,606 (1944). Unpublished results from our laboratory. 1,4 Butynediol does not react analogously; see Johnson, *J. Chem. Soc.*, **1946**, 1014.

[80] Janz and co-workers, *Can. J. Research*, **B25**, 272, 283, 331 (1947); *Chem. Abstracts*, **41**, 6886, 6797 (1947); **42**, 568 (1948).

At the temperature employed, the primary dihydropyridine derivatives spontaneously lose the supernumerary hydrogen atoms.

In order to complete the picture, I would like to mention one other reaction of acetylene which could be expected formally to correspond to that with carbon monoxide, viz., that with sulfur. As you know, this reaction does not lead to an acetylene sulfide, but to a number of sulfur-bearing ring systems, when acetylene[81] is passed over pyrites at 260–300°. The yield is 50%, and about the same result is obtained when a mixture of hydrogen sulfide and acetylene passes over activated alumina at a temperature of 425–450°, *i.e.*, under conditions under which hydrogen sulfide already decomposes markedly into the elements. Indeed, some ethyl mercaptan and ethylthiophene have been observed under such conditions,[82] which may well be due to the formation of hydrogen in the decomposition of hydrogen sulfide. Occurrence of the mercaptan makes it not improbable that acetylene sulfide is the primary product. It can react with acetylene in the following manner, which leads directly to thiophene (I):



(I)

Thiophene can further be expected to be vinylated under these conditions, and α- and β-vinyl thiophene might well be the intermediates, from which the thiophthenes are formed, which are known to be by-products of this thiophene synthesis:

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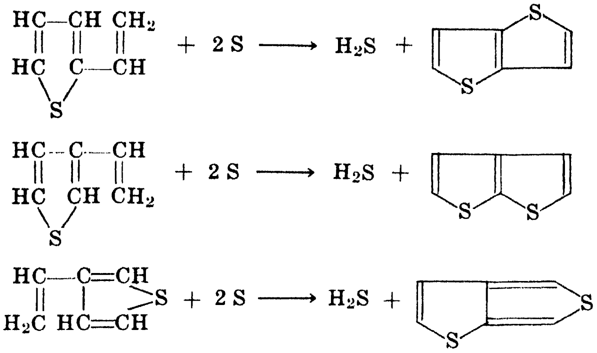
[81] Steinkopf and Kirchhof, *Ann.*, 403, 1 (1914). Steinkopf, *ibid.*, 428, 123 (1921).

[82] Tchitchibabin, *J. prakt. Chem.*, 108, 200 (1924).



We now come to the next major point on our program, a review of the metal derivatives of acetylene and of those acetylene derivatives which possess a terminal hydrogen atom. Not all carbides can be considered as derivatives of acetylene, and if one tries to classify them according to their ability to yield acetylene upon hydrolysis, one obtains the following groups: (*a*) The alkali metals and alkaline earth metals form carbides which give acetylene upon mere contact with water. Only the alkali metals are capable of giving acetylides of the formula $CH\equiv CX$. (*b*) The carbides of the metals of copper and mercury type (copper, silver, gold, mercury) are not attacked by water, but give acetylene upon treatment with acids. (*c*) The carbides of the rare earths upon treatment with water and acids give mixtures of acetylene, hydrogen, ethylene, and higher hydrocarbons. (*d*) Uranium and thorium behave like the rare earths, but their decomposition also leads to methane. (*e*) All other metal carbides give no acetylene at all; outstanding among them are those of beryllium and aluminum which give pure methane upon hydrolysis.

The monoalkali acetylides are formed from the metal and acetylene at 180°C.; above 210° one obtains the dialkali acetylides, by a process of dismutation. Another method employs the reaction of the metal in liquid ammonia at low temperatures,[83] or of a solution of sodamide in liquid ammonia.[84] From the point of view of the synthetic organic laboratory, the alkali acetylides are the most important derivatives, more perhaps than the technically most valuable and most accessible calcium carbide. They are only equalled by the bromomagnesyl derivatives which are obtained by interaction of gaseous acetylene with an ethereal solution of ethylmagnesium bromide. In all circumstances, this reaction leads to a mixture of the mono- and disubstituted product, as is evidenced by the result of further reactions. However, one should not lose sight of the possibility that a disubstitution product may be obtained, even if only the monobromomagnesyl compound was present in the original solution. This can be due to a secondary reaction of the primary reaction product:

$$\mathrm{CH{\equiv}CMgBr} \longrightarrow \mathrm{CH{\equiv}CX}$$

with another molecule of the monobromomagnesyl compound according to the scheme:

$$\mathrm{CH{\equiv}CX + CH{\equiv}CMgBr} \longrightarrow \mathrm{BrMgC{\equiv}CX + CH{\equiv}CH}$$

which would lead to a two-sided end product $\mathrm{XC{\equiv}CX}$. It is interesting in this connection that magnesium carbide shows no resemblance to the bromomagnesyl acetylides; its hydrolysis leads to a mixture of acetylene and methylacetylene, so that Novack has assumed that two different carbides are formed from magnesium turnings and acetylene (or various other carbon compounds, such as carbon monoxide or hydrocarbons) at 500–600°C., the usual method of preparation. Their formulae are C_2Mg and C_3Mg_2.[85]

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[83] Moissan, *Compt. rend.*, 127, 911 (1898).

[84] Picon, *Bull. soc. chim.*, 29, 709 (1921).

The alkali and bromomagnesyl derivatives behave like all other organometallic compounds of the Grignard or zinc alkyl type. The metal can be replaced by alkyl[86] groups—this is the method which is in use for the preparation of alkylacetylenes; it can react with carbon dioxide to give acids, and with aldehydes and ketones to give acetylenic alcohols.[87] Obviously, the same ability to form alkali and bromomagnesyl derivatives applies to all the monoalkylacetylenes so obtained.

Calcium carbide, although it is a true acetylide, is very much less prone to metathetical reactions—perhaps only for reasons of solubility (we shall have to discuss an exception from this rule in the next lecture). Only elementary halogen appears to be able to react with calcium carbide: iodine in liquid ammonia gives diiodoacetylene,[88] and liquid bromine also reacts slowly with the carbide.

Generally speaking, the acetylides of copper, silver, gold, and mercury are still less reactive, as far as metathetical

[85] Novack, *Ber.*, 42, 4209 (1909); *Z. physik. Chem.*, 73, 528 (1910). Irmann and Treadwell, *Helv. Chim. Acta*, 30, 775 (1947), showed that the composition of the magnesium carbide depends on the organic material used in its preparation. Pentane and magnesium vapor give only Mg_2C_3, not MgC_2. Carbon and magnesium do not react with each other between 800° and 1200°.

[86] The bromomagnesyl derivatives do not react with primary alkyl halides, unless they are of the allyl or benzyl halide type. The bromomagnesyl radical can, however, be exchanged for alkyl groups, if alkyl sulfates or sulfonates are employed. Johnson, Schwartz, and Jacobs, *J. Am. Chem. Soc.*, 60, 1882 (1938).

[87] For a very complete survey of this field, see Johnson, *The Chemistry of the Acetylenic Compounds*, Vol. I: *The Acetylenic Alcohols*, Arnold, London, 1946.

[88] Union Carbide and Carbon Corp., U. S. Pat. 2,124,218 (1938); *Chem. Abstracts*, 32, 7058 (1938).

reactions are concerned. They are all more or less explosive. While cupric acetylide forms only at a very low rate, that of monovalent copper precipitates immediately when acetylene is passed through an ammoniacal solution of cuprous chloride. In an analogous manner, silver acetylide is prepared. Both compounds are used for the detection of acetylene and true acetylenic hydrocarbons; but from the point of view of quantitative determination one must be aware that the cuprous compounds often cannot be described by a stoichiometric formula, and that the silver derivatives do not always have the same composition. In this case, two types exist: the true acetylides, *e.g.*, C_2Ag_2, and their crystalline double compounds with silver nitrate.[89] With iodine—one of the few reagents to which these heavy metal acetylides respond—both cuprous and silver acetylides form iodo-substituted acetylenes[84,90]; evidently, the driving force is the fact that the heavy metal iodides are thermochemically favored. One other important reaction, specific—so it seems—to the cuprous compounds, is the oxidation with air or with potassium ferricyanide.[91] It leads to derivatives of diacetylene. Their system appears to have so low a free energy that the cuprous derivative of *tert.* butylacetylene decomposes at 150°C. into metallic copper and di-*tert.* butyldiacetylene.[92]

I hope I have given you a consistent picture of the acetylene system, of its molecular architecture, and of its different modes of reaction. This knowledge will enable us to understand more readily those more complex transformations which will form the subject of our next seminar. It will be particularly devoted to a group of reactions which can be carried out with the alkali acetylides and their copper analogs, and which gives rise to a fairly large number of types of chemicals, some of them of considerable practical and theoretical importance. It will be interesting to compare these two sets of developments, which have taken place independently during the last few years.

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[89] See, for example, Nieuwland and Maguire, *J. Am. Chem. Soc.*, 28, 1029 (1906).

[90] I. G. Farbenindustrie, German Pat. 712,742 (1941); *Chem. Abstracts*, 37, 4406 (1943) and German Pat. 714,312 (1941); *Chem. Abstracts*, 38, 1753 (1944). See also Holleman, *Ber.*, 20, 3080 (1887).

[91] Baeyer, *Ber.*, 18, 2269 (1885). Lespieau, *Ann. chim. phys.*, 11, 281 (1897). Straus, *Ann.*, 342, 224 (1905).

[92] Piganiol, *Acétylène, Homologues et Dérivés.* Masson, Paris, 1945, p. 263.

SECOND LECTURE

We have tried in the first seminar to classify the reactions of acetylene and to relate them to its molecular structure as determined by the methods of physical chemistry. We have studied the stereochemical inferences of the addition of molecules of the type X_2, such as hydrogen, which—in catalytic hydrogenation—converts a disubstituted acetylene into a *cis*-olefin, and halogen, which gives predominantly *trans*-dihalogenoolefins. We have further seen that reagents of the type HX add to acetylenes in the expected manner to give monosubstituted olefins, and that the type HX includes many reagents which were not known to react as easily or at all with the corresponding olefins. The third type of addition is the "molecular" addition, in which two unsaturated systems, that of the acetylene and that of the reagent, saturate each other by a process of association. Such reagents are carbon monoxide, diphenylketene, diazomethane, fulminic acid, and dienes, and we have tried to explain the behavior of sulfur (which gives heterocyclic ring systems) in an analogous way.

It might be useful to elaborate a bit on perhaps the most unusual group of addition reagents HX, *viz.*, the nitrogen compounds. We have seen that secondary aromatic amines under the influence of potassium hydroxide and aqueous solutions of tertiary amines are simply vinylated by acetylene. Also substances like succinimide, phthalimide, and pyrrolidone react in this way.[1] Secondary aliphatic amines show somewhat more complex behavior; they lead first to the *N*-vinyl derivatives, but these add another molecule of acetylene to give:

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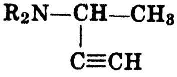
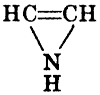
[1] I. G. Farbenindustrie, French Pat. 865,354 (1940); du Pont, French Pat. 883,568 (1940).



$$R_2N\text{—}\underset{\underset{C\equiv CH}{|}}{CH}\text{—}CH_3$$

Simpler amines react in a still more complicated manner. Ammonia has been known to give, over activated alumina at above 300°C., a mixture of heterocyclic compounds[1a]: pyrrole, pyridine, α- and γ-picoline, various dimethylpyridines and α-methyl-β-ethylpyridine. Zinc chloride[2] catalyzes the same reaction at 170–180° under pressure (in liquid ammonia) and gives pyridine and its methyl derivatives; vinylacetylene and its homologs behave similarly.[3] If we recall the mechanism for the formation of thiophene from acetylene and sulfur or hydrogen sulfide, we will assume (formally) that ammonia dissociates and that NH will give acetyleneimine:

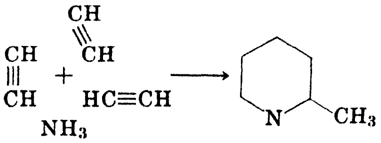


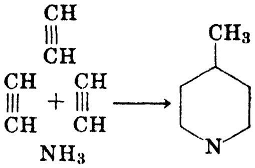
which then reacts with a second molecule of acetylene to form pyrrole. The formation of α- and γ-picoline is also understandable; they are derived from three molecules of acetylene:

[1a] R. Meyer and Wesche, *Ber.*, **50**, 422 (1917). Tchitchibabin, *Chem. Abstracts*, **9**, 2512 (1915). Tchitchibabin and Moshkin, *J. Chem. Soc.*, **126**, 313 (1924); *J. prakt. Chem.*, **107**, 109 (1924). Compare Amiel and Nomine, *Compt. rend.*, **224**, 483 (1947)—silicon dioxide -zinc sulfate catalyst.

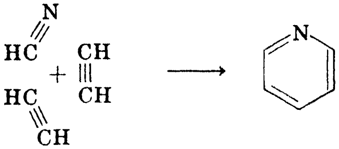
[2] I. G. Farbenindustrie, French Pat. 800,499 (1936).

[3] du Pont, Brit. Pat. 516,586 (1940); *Chem. Abstracts*, **35**, 6267 (1941).





It is obvious that acetylene and α-picoline can give the β-vinyl derivative, which is then hydrogenated. An interesting problem is posed by the occurrence of pyridine; I believe that one can explain it only by assuming that hydrogen cyanide is formed to a certain extent from ammonia and acetylene—a well-known[4] high-temperature reaction—and that this acid undergoes a diene reaction of the type known for the case of cyanogen which we mentioned in the last seminar:



It might well be the case that the actual carrier of this reaction is vinylacetylene, a dimeride of acetylene which will occupy our attention in the next seminar, and possibly the same intermediate must also be assumed in the other cases in which heterocyclic compounds are formed from acetylene.[4a]

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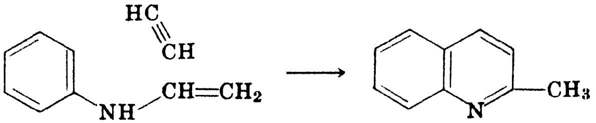
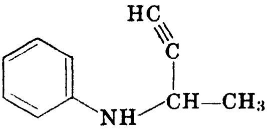
[4] See, for example, Mixter, *Am. Chem. J.*, 10, 299 (1888); Amiel and Nomine, *Compt. rend.*, 224, 483, (1947).

[4a] For the formation of thiophenes from dienes, see Coffman, *Chem. Abstracts*, 41, 2086 (1947).

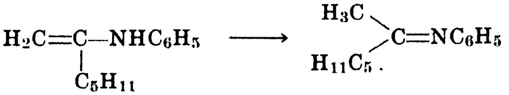
From aniline, too, one can obtain a vinyl derivative, using copper, silver, or mercury salts as catalyst. However, the reaction does not stop at this point, and by the reaction:



α-methylquinoline is formed.[5] One might well assume a mechanism of the sort established for secondary aliphatic amines, which would lead first to:



This would then cyclize by hydrogen transfer in the usual manner. The primary product, the *N*-vinyl compound, has two other possibilities of stabilization, both showing the astounding reactivity of these *N*-vinylated primary amines. Pentyl-acetylene[6] gives the anil of methyl pentyl ketone:



$$\underset{\displaystyle C_5H_{11}}{H_2C{=}\overset{}{C}}\text{—}NHC_6H_5 \longrightarrow \begin{matrix}H_3C\\ H_{11}C_5\end{matrix}\!\!>\!C{=}NC_6H_5 .$$

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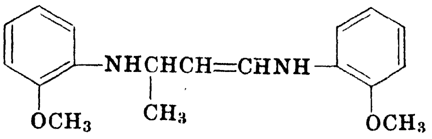
[5] See, for example, Koslow and co-workers, *Chem. Zentr.*, **1937**, **I**, 869, 4101; **1937**, **II**, 4636; **1939**, I, 619, and further papers. Tchitchibabin [*Chem. Abstracts*, **9**, 2512 (1915)] observed indole (the analogon of pyrrole in the reaction of acetylene and ammonia) and 4-methylquinoline, using aluminum oxide at 360–420°. Majima, Unno, and Ono [*Ber.*, **55**, 3854 (1922)] observed indole and carbazole at 700° with a nickel catalyst (carbazole is a pyrolysis product of aniline alone).

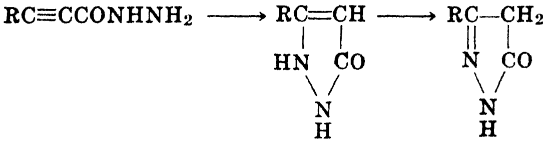
[6] Loritsch and Vogt, *J. Am. Chem. Soc.*, **61**, 1462 (1939).

and *o*-anisidine[5] a "bimolecular" reaction product which was shown to be:



1,3-di-(*o*-anisidino)-butene-(1). In this case the *N*-vinylanisidine does not react with a second molecule of acetylene, but rather with one of *N*-vinylanisidine.

The hydrazines with their free amino group can evidently also add to acetylenic triple bonds. One will thus understand that the hydrazides of acetylenic acids isomerize to pyrazolones:[7]



3-Alkyl-5-pyrazolone

Apart from these addition reactions we have seen that acetylenes with a terminal hydrogen are also capable of very characteristic substitution reactions. We mentioned the substitution by halogen and the Mannich reaction with formaldehyde and dialkylamines, which may be either a reaction of the acetylene with a dialkylaminomethanol or of the dialkylamine with an acetylenic alcohol primarily formed. This would correspond to a known reaction of asymmetrically disubstituted ethylenes (see page 2):

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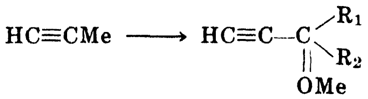
[7] Moureu and Lazennec, *Compt. rend.*, 142, 1534 (1906); 143, 1239 (1906).

$$R_2C{=}CH_2 \rightarrow R_2C{=}CHCH_2OH$$

However this may be, the reaction is due to the reactivity of the hydrogen, and we have already agreed that the acetylenes can be considered as pseudo acids—which explains why all these reactions take place in an alkaline medium, *i.e.*, under conditions under which an ion or a metal derivative can be formed. Indeed, Reppe has made the surprising observation[8] that copper acetylide can react with aldehydes and ketones according to the scheme:



which leads to acetylenic alcohols. Equally silver, mercury, and gold acetylides can be used or these metals in a finely divided state in which they form acetylides. One has to work under pressure (3 atmospheres and higher) and at 100°C. It is rather surprising that this reaction does take place when one considers that—as we stated in the last seminar—these heavy metal acetylides do not lend themselves to substitution under laboratory conditions, and that, *e.g.*, alkylation is possible only if one uses alkali acetylides or the bromomagnesyl derivatives. But I wonder whether, under suitable operative conditions, it may not be possible to carry out *all* these reactions with heavy metal acetylides.

Most of the work carried out by Reppe and his school has been concerned with formaldehyde; it undoubtedly represents one of the finest pieces of organic research carried out in recent years (Table I). Under well-defined condi-

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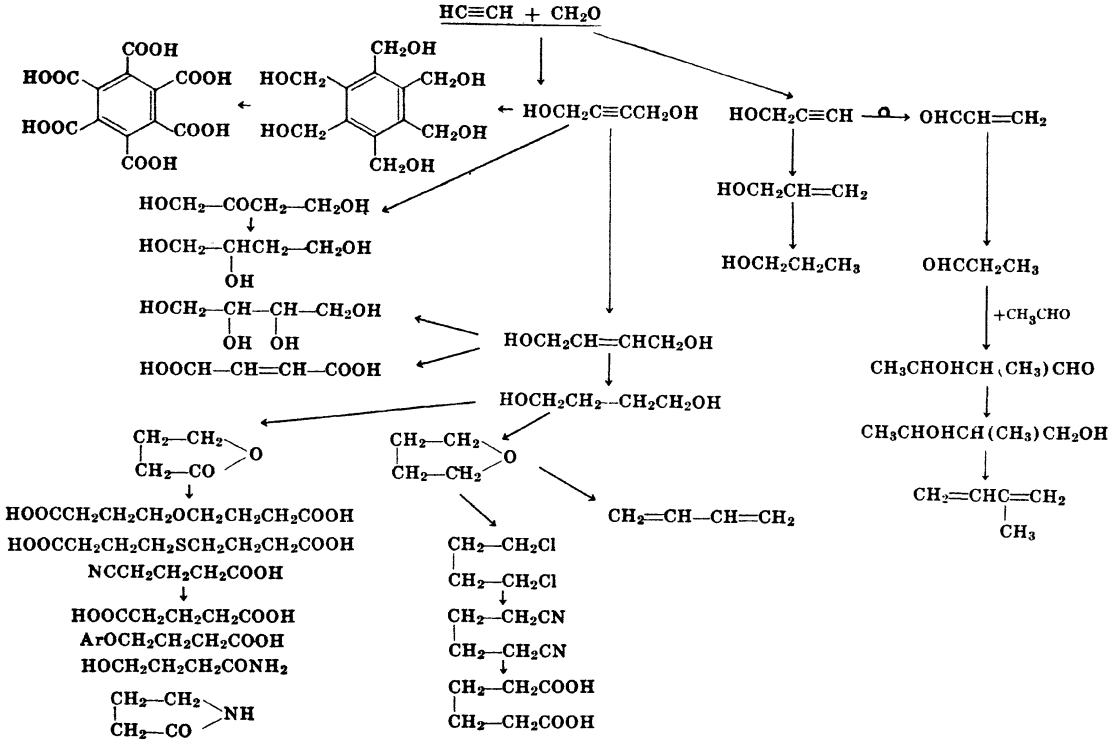
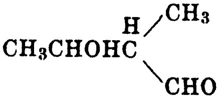
[8] French Pat. 841,500 (1939). The work of Reppe is reported from *Advances in Acetylene Chemistry*, Technical Report from Reconstruction Finance Corporation, Office of Rubber Reserve, Research and Development Section, July 25, 1945.

TABLE I. REPPE



tions two molecules of formaldehyde (in the form of its 30% aqueous solution)—it is a distinct advantage of this particular method that it does not demand the absence of water—give with acetylene, in 98% yield, 2-butyne-1,4-diol, $HOCH_2C{\equiv}CHCH_2OH$. The reaction is carried out in a tower, using copper acetylide on a carrier and dilute acetylene at 98–100°C. and 3 atmospheres pressure. One obtains a 35% solution of the butynediol, and the considerable heat of reaction (24 kcal. per mole) is taken off by the water which is partly evaporated.

The butynediol has been found most attractive as a possible source of butadiene, a source that makes butadiene independent of the otherwise required C_4 compounds of the petroleum industry. One hydrogenates the aqueous solution with nickel under 200 atmospheres pressure (exothermicity, 60 kcal. per mole) and dehydrates the 1,4-butanediol formed. It has proven advantageous to carry out this dehydration in two steps, the first of which leads to tetrahydrofuran. This is formed when the aqueous solution of the diol is heated with some phosphoric acid at 300°C. under 100 atmospheres pressure, and can be separated easily due to its low boiling point (65°C.) ; it is converted into butadiene over phosphate catalysts, as alkali hydrogen phosphate or butylammonium phosphate, at 260–280°C. However, this is not the only interesting end product of the reaction between acetylene and formaldehyde. It is obvious that one can produce by this reaction propargyl alcohol (using an excess of acetylene), which can be hydrogenated to allyl alcohol (from which glycerol can be made) and propyl alcohol. The latter becomes an easily available material, and an old injustice is thus remedied, which gave propyl alcohol only a few lines in small print in textbooks between ethyl and butyl alcohols, its easily accessible and well-studied relatives. It is most interesting that the same hydrogenation in an acid medium leads to propionaldehyde only, undoubtedly due to the fact —to which we will have to return later—that propargyl alcohol is isomerized by acids to $HC_2{=}C{=}CHOH$, or rather acrolein. Propionaldehyde (also made from propyl alcohol by dehydrogenation) can react with acetaldehyde to give a mixed aldol, the 2-methyl-3-hydroxybutanal:



$$CH_3CHOH\overset{H}{C}\begin{matrix}\nearrow CH_3\\ \searrow CHO\end{matrix}$$

Hydrogenation leads to a methylbutanediol, which can be dehydrated to isoprene, the parent substance of natural rubber.

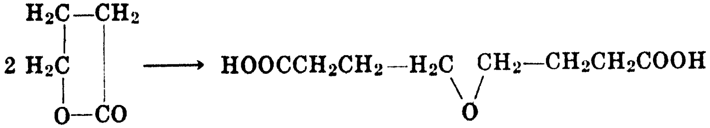
Butynediol, too, can be converted into a fair number of other transformation products. It trimerizes to hexamethylolbenzene and is thus an excellent source for mellitic acid. Hydration converts it in the normal way to 2-butanone-1,4-diol, which can be further hydrogenated to a glycerol homolog, butane-1,2,4-triol.[8a] The butynediol can also be hydrogenated to 2-butene-1,4-diol, which can be oxidized (hydroxylated) to erythritol; it is interesting to note at this point that hypochlorous acid or hydrogen peroxide gives the racemic form, permanganate or osmium tetroxide with potassium chlorate, the meso form. Oxidation in the gas phase leads to maleic acid—the same is true for dihydrofuran, the dehydration product of 2-butene-1,4-diol. It is a common, though surprising, feature that catalytic oxidation of such substances does not attack the double bond.[9]

2-Butene-1,4-diol is a homolog of allyl alcohol and like the latter can be used as philodienic component in Diels-Alder syntheses.

[8a] I. G. Farbenindustrie, Belgian Pat. 449,639; *Chem. Abstracts*, 42, 212 (1948).

[9] Crotonaldehyde, for example, was known to give maleic anhydride upon catalytic oxidation in the vapor phase.

Catalytic dehydrogenation of butane-1,4-diol does not lead to succinic dialdehyde—which would be a most interesting starting material for all kinds of syntheses—but rather to its isomer, γ-butyrolactone, which owes its formation to an intramolecular oxidation-reduction reaction. This lactone is an unusually active substance. Caustic alkali gives under suitable conditions the sodium salt of dipropylether-ω,ω′-dicarboxylic acid:



and the analogous reaction takes place with sodium hydrosulfide; both acids can be used in the making of polyamides of the nylon type. Another diacid which now becomes easily available is glutaric acid; its nitrile, γ-cyanobutyric acid, is formed from the lactone and sodium cyanide, and its dinitrile can be converted to 1,5-pentamethylenediamine, another component for polyamides. Phenolates give the salts of γ-aryloxybutyric acids, ammonia γ-hydroxybutyramide, or α-pyrrolidone. We have already mentioned the vinylation of the latter which gives a hard, colorless, water-soluble polymer, used by the Germans as a substitute for blood plasma (Periston).

Some words may not be out of place on the possible uses for tetrahydrofuran. It is a good solvent for polyvinyl compounds, including rubber and Buna S,[10] and—as we will see in the next seminar—for acetylene in the process of making cyclooctatetraene. Its reaction with hydrochloric acid gives, among other possible products, 1,4-dichlorobutane, which can be converted by reaction with sodium cyanide into adiponitrile. Thus this acid and hexamethylenediamine become available from acetylene and formaldehyde, and one becomes independent of their classical source, cyclohexanol, and therefore of coal tar (phenol) or petroleum (cyclohexane). It might be added that the easy availability of such diols as butane-1,4-diol makes possible another type of high polymer, which is similar in principle to the nylon-type polyamides. The reaction of such diols with diisocyanates gives polyurethans; of course, the diisocyanates are made from the corresponding diamines and phosgene.

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[10] I. G. Farbenindustrie, French Pat. 850,453 (1939); *Chem. Abstracts*, 36, 1794 (1942).

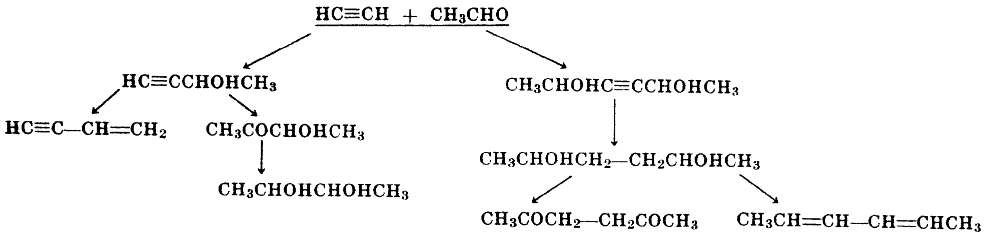
Another interesting polymer, either soft and resinlike or solid and rubberlike, is made directly from tetrahydrofuran and certain metallic salts, which, as in the case of ethylene oxide, open the ring and transform it into a unit in a long chain:

$$\text{—O—CH}_2\text{—CH}_2\text{—CH}_2\text{—CO—}$$

This whole scheme of reactions becomes more impressive if one realizes that formaldehyde is not the only partner which reacts with acetylene, but that other aldehydes and ketones can be used equally well. Aromatic and α,β-unsaturated aldehydes react in the same way as aliphatic ones.

Acetaldehyde may further illustrate the possibilities of this method (see Table II on page 48). 3-Butyne-2-ol, $CH_3CHOHC\equiv CH$, can be dehydrated to vinylacetylene, hydrated to butane-2-ol-3-one, and the latter hydrogenated to the interesting 2,3-butylene glycol, which so far has been a fermentation product. The "bimolecular" reaction product, 3-hexyne-2,5-diol, $CH_3CHOHC\equiv CCHOHCH_3$, can be hydrogenated to 2,5-hexanediol which is dehydrogenated to acetonylacetone and dehydrated to 1,4-dimethylbutadiene.

TABLE II. REPPE



According to available reports, the reaction with ketones is not as satisfactory; it is therefore rather curious that, parallel with Reppe's work, another reaction has been developed, which is especially suitable for the condensation of ketones with acetylene and which has certain other obvious advantages in its favor as well as some disadvantages, as compared with Reppe's method. It has also been used for the production of a fairly large number of interesting derivatives, and it, too, has made easily available some products which so far have been mere laboratory curiosities. In order to evaluate this reaction properly, we will have to turn back the pages of the history of chemistry to some early work of Russian scientists. Kazarian[11] observed that one can condense acetone with acetylene to 3-methyl-1-butyne-3-ol, $(CH_3)_2C(OH)C{\equiv}CH$, if one adds acetone to a mixture of calcium carbide and potassium hydroxide suspended in benzene. The reaction is not satisfactory because it is slow —undoubtedly, one reason is the difficulty of obtaining calcium carbide in a sufficiently finely divided form—and, therefore, sometimes leads to a considerable number of side reactions, such as the self-condensation of acetone. Favorski had already observed in 1902[12] that one can obtain consistent results if one passes acetylene into a mixture of acetone, potassium hydroxide, and benzene or ether at a low temperature. Here too the method has proven to be not very satisfactory, but one can observe that ether is a better solvent than benzene—and so a systematic study was suggested of the influence of the solvent on the course of the reaction, *i.e.*, on both the rate and the yields. Zeltner and Genas were the first to observe that, generally, ethers and ether-oxygen-containing substances and nitrogen compounds such as amines are favorable media, and in particular that methylal permits the reaction to proceed with great speed at a low temperature (—10°) and to give yields of 90% and better.[13] This study was extended by Weizmann and his students[14] and led to the conclusion that all substances containing the groups O—C—O and O—C—C—O are eminently suitable, *i.e.*, acetals, cyclic or acyclic, derived from aldehydes or ketones, and the dialkyl ethers of ethylene glycols. These substances are easily available and, using one with a suitable boiling point, one can dispense with methylal which, due to its high volatility, is not too agreeable to handle. If one adds potassium hydroxide to these solvents and heats them up, the hydroxide is very finely dispersed and the suspension absorbs acetylene with great rapidity. If one then adds acetone, the strongly exothermic reaction leading to methylbutynol takes place at —10 to —15°C. with almost quantitative yield. There can be no doubt that acetylene does actually form potassium acetylide[15]; one can treat the whole product with carbon dioxide and obtain—in addition to potassium carbonate—the potassium salts of propiolic acid and (we will return to this point) of acetylenedicarboxylic acid.[16] Indeed, the product of the reaction with acetone is not methylbutynol but its potassium derivative, which is hydrolyzed when, in the course of treatment, water is added to the mixture; thus we have here a means of producing potassium acetylide which does not rely on a solution of the alkali metal in liquid ammonia. It is not necessary to work under strict exclusion of even traces of water. This was to be expected, as the formation of potassium acetylide obviously implies the liberation of water. As a matter of fact, one can use ordinary potassium hydroxide, which contains 10–13% water, and the only point to observe is that one has to use an excess of the hydroxide (double the theoretical amount) of which only half is converted into the acetylide, while the other half serves to tie up the liberated water and thus to prevent the reversal of the reaction, *i.e.*, the normal hydrolysis of an organo-alkali compound.

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[11] Kazarian, *Chem. Abstracts*, **29**, 3978 (1935). Gambarian and Kazarian, Russian Pat. 41,516 (1933); (*Chem. Zentr.*, **1935, II**, 3702). See Zakharova, *Chem. Abstracts*, **32**, 2506 (1938).

[12] Favorski, *J. Gen. Chem.*, **32**, 356, 652 (1902). A recent survey has been given by this author in *Bull. Acad. Sci., U.R.S.S., Classe sci. chim.*, **1940**, 181 [*Chem. Abstracts*, **37**, 3146 (1943)]. Compare also *Chem. Abstracts*, **37**, 4049 (1943); **36**, 3147 (1942); **35**, 5092 (1941).

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[13] Zeltner and Genas, Brit. Pat. 544,221 (1942); U. S. Pat. 2,345,170 (1944); *Chem. Abstracts*, 38, 4273 (1944).

[14] Weizmann, Brit. Pats. 573,527 (1945), 580,921 (1946), 580,922 (1946); *Chem. Abstracts*, 41, 2429, 2066 (1947). Compare I. G. Farbenindustrie, Belgian Pat. 449,275; *Chem. Abstracts*, 42, 200 (1948).

[15] This was known from Lange's German Pat. 712,742 (1941); *Chem. Abstracts*, 37, 4406 (1943).

[16] E. Bergmann and D. Herman, unpublished results. That the condensation does not involve the formation of an enolate of acetone (thus making it a variation of Merling's classical method) can also be concluded from the fact that benzophenone (which is not enolizable) undergoes the same reaction. Babayan, *Chem. Abstracts*, **35**, 2858 (1941).

What is it that makes the acetals and glycol dialkyl ethers capable of activating potassium hydroxide to such an extent that it reacts with acetylene as vigorously as, or more vigorously than, *e.g.*, a solution of metallic potassium or sodium in liquid ammonia? One might say that it is a purely physical effect, which gives the hydroxide a large surface; but I prefer the explanation that the activation is due to the formation of a molecular compound of inner-complex nature,[17] in which the hydroxide loses some of its normal characteristics and acquires some new ones. It appears significant to me that in this respect neither lithium nor sodium hydroxide behave analogously. We have here one of the few cases in which sodium and potassium compounds are not interchangeable; there are a few more known to the organic chemist. The oldest one is the reaction of phenolates with carbon dioxide: the potassium compound favors the formation of *p*-hydroxybenzoic acid, the sodium compound that of salicylic acid.

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[17] Ethers and acetals form molecular compounds with magnesium halides (Menschutkin, quoted in Beilstein, Vol. I, p. 574; Vol. II, p. 604), which have the character of nonelectrolytes (Weinland, *Einführung in die Chemie der Komplexverbindungen*, Enke, Stuttgart, 1919, p. 224.

Another interesting example has recently[18] been discovered in the case of phenylacetylene. Its potassium derivative proved very refractory in reactions with various esters, while both the lithium and the sodium derivatives showed a ready response. However, they did not always form identical reaction products: with acetyl chloride or acetic anhydride the sodium derivative gave phenylbenzoylacetylene, while the lithium analog gave bis-(phenylethinyl)-methylcarbinol. With cinnamic anhydride, the same differential reactivity was observed; with ethyl cinnamate, however, as well as with ethyl phenylpropiolate, both metallo-organic compounds led to the normal tertiary alcohols.

One can expect that the system potassium hydroxide–acetylene–specific solvent would show all the reactions of potassium acetylide. This is true with one limitation; since we employ an excess of the hydroxide and since this excess contains water, substances like alkyl halides are more easily hydrolyzed by this hydrated excess than condensed with the acetylide. The same effect also imposes a limitation on the choice of carbonyl compounds which can condense with acetylene to acetylenic alcohols under these conditions. All ketones react easily—and in this respect the new method favorably supplements the Reppe reaction with aldehydes—even quite complicated ones such as cyclohexanone, acetophenone, decalone,[18a] or 3-methyl-3-butanol-2-one.[19]

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[18] Nightingale and Wadsworth, *J. Am. Chem. Soc.*, 69, 1181 (1947).

[18a] Nikitin, *Chem. Abstracts*, 40, 4700 (1946).

[19] Nikitin, *Chem. Abstracts*, 40, 4665 (1946). For other hydroxyketones see Nazarov and Torgov, *Chem. Abstracts*, 38, 4595 (1944), and Onishchenko, *ibid.*, 39, 694 (1945).

All those aldehydes, however, are unsuitable, *i.e.*, give insignificant yields, which are easily resinified or forced to autocondensation by the hydroxide; practically, this means that no straight-chain aldehydes should be employed.[19a] Aldehydes, however, which are branched in the α-position (such as isobutyraldehyde) and aromatic aldehydes react in the expected manner.[20]

The reaction is not limited either to the ratio 1 : 1 of the reagents. Acetone does give methylbutynol at —10°C. if equimolecular amounts of the reagents are used. At elevated temperatures, *i.e.*, at 20°C. and with the ratio 1 : 2, equally good yields of the corresponding diol, the tetramethylbutynediol are formed.[21] Indeed, if one treats methylbutynol, obtained at —10°C., with potassium hydroxide and a second molecule of a carbonyl compound—be it acetone or any other representative of the class which we have just defined —at about 20°C., a diol is formed; and, when potassium methylbutynolate is kept at 20°C. for some time, it disproportionates to acetylene and the potassium derivative of acetylenic glycol. Conversely, the diol is not stable against alkali at elevated temperatures. Potassium or magnesium carbonate decomposes it at 100° into methylbutynol and acetone, and potassium hydroxide even to acetylene and two molecules of acetone. Equally, of course, methylbutynol is split at 100° by alkali into acetone and acetylene. Indeed, the tendency to reverse the synthesis is characteristic for

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[19a] *Seguin* [*Bull. soc. chim.*, 12, 948 (1945)] has shown recently that addition of sodamide suppresses the undesirable side reactions and permits the preparation of secondary acetylenic alcohols from straight-chain aldehydes in satisfactory yields.

[20] The other methods (sodium acetylide in liquid ammonia; bromomagnesyl acetylides) are, of course, equally applicable to aldehydes and ketones.

[21] See also Babayan and co-workers, *Chem. Abstracts*, 34, 2788 (1940); 35, 2858 (1941). Bruson and Kroeger, U. S. Pat. 2,250,445 (1941); *Chem. Abstracts*, 35, 6974 (1941).

TABLE III. WEIZMANN

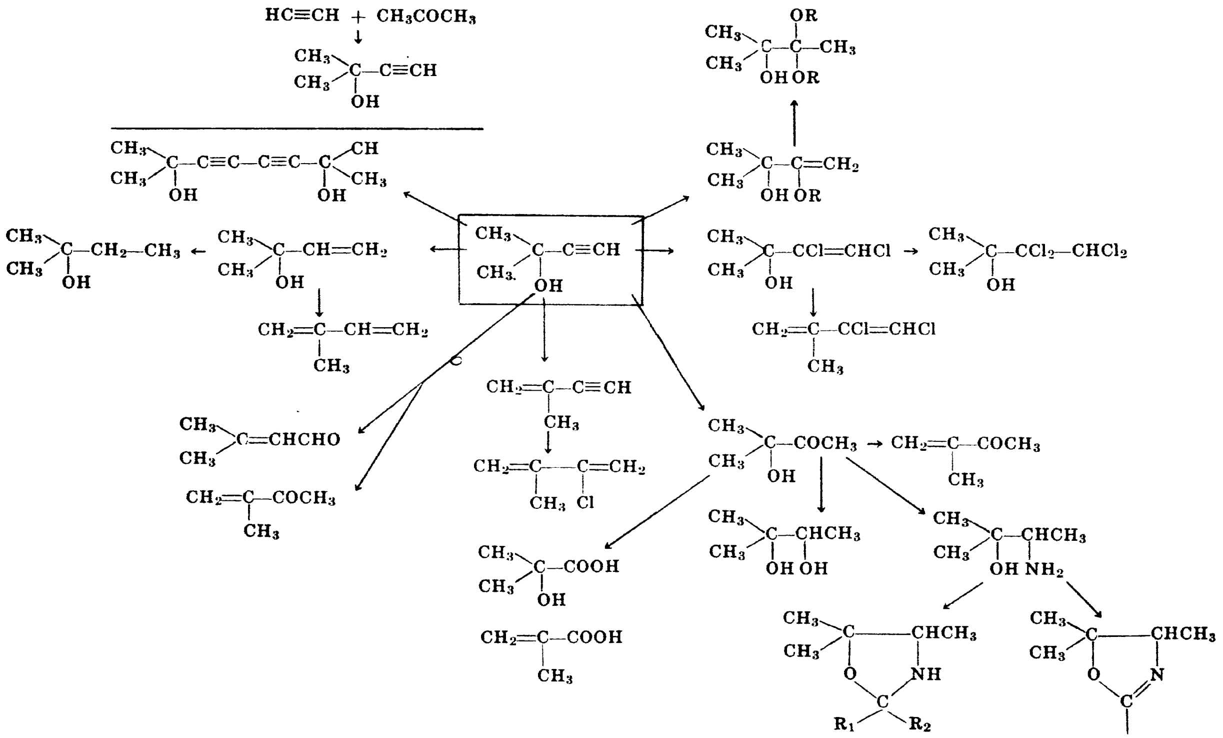
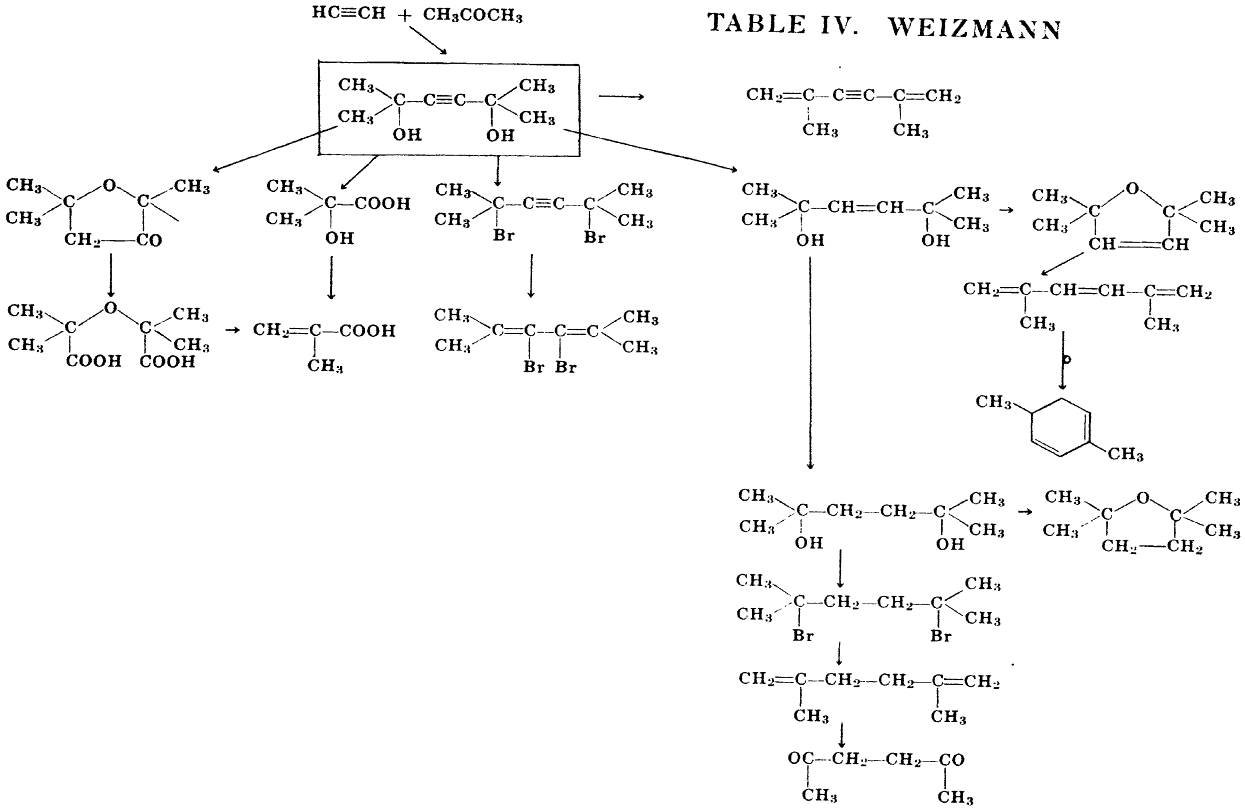


TABLE IV. WEIZMANN



these alcohols and may be exploited for their quantitative determination in mixtures.

A fair number of these two types of acetylenic carbinols have been prepared and the possibilities of their transformations studied. Let us try to survey them (Tables III and IV). Like all true acetylene derivatives, the alkylbutynols can undergo a bimolecular dehydrogenation if air is passed through their solution or suspension in ammoniacal cuprous chloride solution.[22] Thus, diacetylenic glycols are obtained which offer, in turn, a variety of further transformations. The acetylenic bond can add all those reagents which we discussed in the last seminar—as long as the addition does not require alkali hydroxide as catalyst at temperatures above 100°. Alcohols can be added in the presence of mercuric oxide and boron trifluoride to give, via the enol alkyl ethers, acetals of hydroxy ketones[23]; acids lead to the diacyl derivatives of these hydroxy ketones.[24]

Chlorine gives a dichloride, which can be dehydrated to the interesting dichloroisoprene, and further a tetrachloride.[25] Toward bromine, methylbutynol is strangely refractory. Hydrogen is added in two stages to give methylbutenol[26] and tertiary amyl alcohol, successively. It is not easy to stop the strongly exothermic reaction at the olefin stage, because with most catalysts the rates of reaction with the first and the second hydrogen molecules are not sufficiently different, unless one uses palladium deposited on barium sulfate, preheated at 600° (see page 3). This is important, as methylbutenol is the given starting material for the synthesis of isoprene, which is formed upon catalytic dehydration in the vapor phase in the presence of activated alumina. However, these strictures are not necessarily required. One can dehydrate dialkylvinylcarbinols in the liquid phase[27] if one heats them with a small amount of such salts as anilinium hydrochloride or hydrobromide or toluene-*p*-sulfonate. What one actually does is to use a buffered acid—still, the method is quite remarkable because it is specific for these olefinic alcohols. Neither the corresponding acetylenic nor the fully hydrogenated tertiary alcohols are dehydrated under these mild conditions, and one can thus obtain pure isoprene even from a mixture of methylbutenol with methylbutynol and methylbutanol, which is only difficultly resolved as their boiling points are in close proximity to each other.

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[22] Salkind and co-workers, *Ber.*, **69**, 128 (1936); *Chem. Abstracts*, **31**, 4283 (1937); **33**, 8569 (1939); **34**, 3719 (1940).

[23] Hennion and co-workers, *J. Am. Chem. Soc.*, **62**, 653 (1940); **64**, 1220 (1942). See also *ibid.*, **56**, 1130, 1384, 1802 (1934); **57**, 2006 (1935); **58**, 80, 1658 (1936). Nazarov, *Chem. Abstracts*, **36**, 742 (1942).

[24] Hennion and co-workers, *J. Am. Chem. Soc.*, **62**, 653 (1940); **64**, 1220 (1942). See also *ibid.*, **56**, 1130, 1384, 1802 (1934); **57**, 2006 (1935); **58**, 80, 1658 (1936). Nazarov, *Chem. Abstracts*, **36**, 742 (1942); Nazarov and Nagibim, *ibid.*, **37**, 5368 (1943).

[25] Hennion and Wolf, *J. Am. Chem. Soc.*, **62**, 1368 (1940). Petrov, *Chem. Abstracts*, **38**, 1467 (1944).

[26] See Campbell and Campbell, *Chem. Revs.*, **31**, 77 (1942).

As a matter of fact, in some ways methylbutynol and its homologs do not behave as one would expect of tertiary alcohols. They can be esterified most easily and the esters are stable—stable enough to permit the normal reactions of the acetylenic system.[28] They can be converted into the tertiary chlorides,[29] and the latter undergo a type of reaction which is of theoretical interest and will occupy our attention still further. When they are brought into contact with potassium acetate, they give the normal esters. In the presence of silver acetate, however, rearrangement occurs to a certain extent, as it is known from analogous compounds in the olefinic series. The chloride can react as if it had the anionotropic formula:

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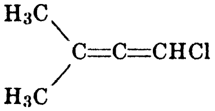
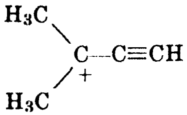
[27] Weizmann, Brit. Pat. 577,364 (1946); U. S. Pat. 2,381,148 (1945); *Chem. Abstracts*, **40**, 346 (1946).

[28] See, for example, Nazarov, *Chem. Abstracts*, **33**, 5682 (1939); and (for the hydration of the triple bond in the esters) McGill, U. S. Pat. 2,198,172 (1940); *Chem. Abstracts*, **34**, 5463 (1940).

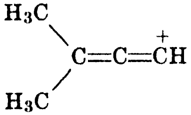
[29] Favorskaja and co-workers, *Chem. Abstracts*, **33**, 9281 (1939); **34**, 7844 (1940).



or more correctly, the positive ion:



which is obviously formed in contact with silver acetate, reacts as:



so that a 3-acetoxy-1,1-dimethylallene is one of the main products of this reaction, described recently by Zakhanova.[30]

Equally, in dehydration experiments, the alkylbutynols behave unexpectedly. The normal catalyst for such vapor phase dehydrations, activated alumina, dismutates the molecule to acetylene and the ketone from which it had been made,[31] and only certain phosphate-type catalysts on only certain very narrowly limited carriers permit satisfactory dehydration to isopropenylacetylene in the case of methylbutynol and to its homologs if homologs of that acetylenic alcohol are the starting materials.[32] Of course, if unsymmetrical ketones are employed, two isomeric vinylacetylenes are possible, for example, from 3-isobutylbutyn-3-ol:

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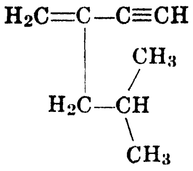
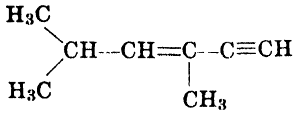
[30] Zakhanova, *Chem. Abstracts,* **40,** 4654 (1946).

[31] Thompson and Margnetti, *J. Am. Chem. Soc.,* **64,** 573 (1942). Vaughn, U. S. Pat. 2,197,956 (1940); *Chem. Abstracts,* **34,** 5461 (1940). Rupe and Rinderknecht, *Ann.,* **442,** 61 (1926). Urion, *Ann. chim.,* **1,** 12 (1934). Thompson, Burr, and Shaw, *J. Am. Chem. Soc.,* **63,** 186 (1941).





These vinylacetylenes will be one of the subjects of the next seminar, and I would therefore—without going into details of operation and mechanism—only mention one reaction, which is necessary to round off the picture, that with hydrochloric or hydrobromic acid in the presence of cuprous and ammonium chlorides. In effect, these acids add to the triple bond and give homologs of chloroprene[33] which, like the parent substance, are capable of polymerization and copolymerization to rubbers. They have now become easily available substances.

Phosphate catalysts also catalyze another type of reaction of the alkylbutynol compounds, which again has its analogon in the scheme of Reppe we have discussed. They isomerize the alkylbutynols; from methylbutynol the interesting dimethylacrolein is obtained. In view of the abovementioned observation of Zakhanova, one will explain this isomerization by a migration of the hydroxyl in the unsaturated triad system; the enol thus formed stabilizes by ketization. I said the aldehyde is interesting; not only because it opens a new way to such substances as dimethylacrylic acid, which has been used in certain copolymers (it was until now only available with reasonable yields from mesityl oxide and hypochlorite[34]), but also because it can condense with malonic acid to a higher unsaturated acid, and with itself to give a dimethyl C_8 aldehyde and a trimethyl C_{12} aldehyde, which contain the skeleton of geraniol and farnesol, respectively, and lead directly into the series of vitamin A.[35]

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[32] E. Bergmann and Wilder, unpublished results.

[33] Carothers and co-workers, *J. Am. Chem. Soc.*, 54, 4071 (1932); 55, 1624 (1933). Backer and Blaas, *Rev. trav. chim.*, 62, 785 (1942). Sargent and co-workers, *J. Am. Chem. Soc.*, 64, 2692 (1942). Favorski, Russian Pat. 31,016 (1932); *Chem. Zentr.*, 1934, I, 2488.

However, from a theoretical point of view, the isomerization reaction is somewhat complicated by the fact that dimethylacrolein is not the only product. It is accompanied by methylisopropenyl ketone, and it is possible to direct, by proper selection of the catalyst type and of the operating conditions, the reaction of the methylbutynol predominantly toward formation of one or the other isomer, or the dehydration to isopropenylacetylene. It is quite possible to assume that the unsaturated ketone owes its formation to a two-step reaction: (*a*) the dehydration to that acetylenic hydrocarbon, and (*b*) the hydration of the acetylenic bond by the water split off in the first step. Indeed, one can hydrate, in the classical manner, isopropenylacetylene to isopropenylmethylketone. But this is not possible—as far as we know—with phosphates as catalysts. One will have to assume an intramolecular mechanism even if one cannot easily express the mechanism by the reaction formulae of classical organic chemistry.[36] Such cases are by no means unknown. Diphenylacetaldehyde, for example, isomerizes under the influence of sulfuric acid to desoxybenzoin.[37]

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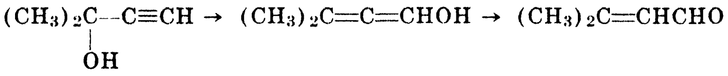
[34] Fourneau and Florence, *Bull. soc. chim.*, 41, 1518 (1927). E. Bergmann, Taubadel, and Weiss, *Ber.*, 64, 1493 (1931).

[35] Fischer and Loewenberg, *Ann.*, 494, 263 (1932). Bernhauer and Woldan, *Biochem. Z.*, 249, 199 (1932). Euler and Klussmann, *Chem. Zentr.*, 1932, II, 2201. Fischer and Marschall, *Ber.*, 64, 2825 (1931).

Whatever the mechanism of the reaction may be, our observation brings to an end an old discussion, *viz.*, whether acetylenic alcohols isomerize under the influence of acids to aldehydes or ketones. Meyer and Schuster[38] have shown that certain, especially aromatically substituted, acetylenic alcohols of the general type $R_2C(OH)C{\equiv}CR$ isomerize under the influence of acidic reagents to α,β-unsaturated ketones $R_2C{=}CHCOR$,[39] a reaction which can be easily explained if one assumes an anionotropic rearrangement to an intermediate of the structure $R_2C{=}C{=}C(OH)R$.[39] In the case of an acetylenic alcohol with a terminal hydrogen, the same mechanism would lead to an aldehyde, for example:



$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}C{\equiv}CH \rightarrow (CH_3)_2C{=}C{=}CHOH \rightarrow (CH_3)_2C{=}CHCHO$$

and Rupe and Kambli[40] thought that they had achieved this rearrangement in many cases by means of 85% formic acid. Fischer and Loewenberg[41] and Hurd and Christ,[42] however, proved that the products obtained were the isomeric α,β-unsaturated ketones:

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[36] Experiments with labeled methylbutynol would be desirable; they would permit a decision as to whether the isomerization involves the migration of methyl groups.

[37] Daniloff and Venus-Danilova, *Ber.*, 59, 377, 1032 (1926). Venus-Danilova and Kazimirova, *Chem. Abstracts*, 42, 110 (1948). Pines and Ipatieff, *J. Am. Chem. Soc.*, 69, 1337 (1947).

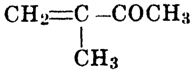
[38] Meyer and Schuster, *Ber.*, 55, 819 (1922).

[39] The only exception appears to be the isomerization of 2-methyl-3-nonyne-2-ol to 2-methyl-2-nonene-4-one; Gredy, *Ann. chim.*, 4, 5 (1935).

[40] Rupe and Kambli, *Helv. Chim. Acta*, 9, 672 (1926).

[41] Fischer and Loewenberg, *Ann.*, 475, 183 (1929).

[42] Hurd and Christ, *J. Am. Chem. Soc.*, 59, 118 (1937). See also Rupe and Hirschmann, *Helv. Chim. Acta*, 14, 687 (1931). Davies, Heilbron, Jones, and Lowe, *J. Chem. Soc.*, 1935, 586. Dimroth, *Ber.*, 71, 1333 (1938). Rupe and Kuenzi, *Helv. Chim. Acta*, 14, 701 (1931).



$$CH_2{=}C(CH_3){-}COCH_3$$

There appear to be only a very few cases in which the aldehydes are also formed in the liquid phase,[43] and catalytic isomerization in the vapor phase appears to be the only method for achieving that end.

Of practical importance is the hydration of the alkyl butynols to the corresponding alkyl butanolones.[44] These not only give the normal reactions of methyl ketones—of which I might mention that with hypochlorite which opens a new route to hydroxyisobutyric acid[45] and, therefore, to methacrylic acid and their homologs, they also are capable of easy dehydration, leading again in the simplest case to methylisopropenylketone.[46] This like the similarly constituted methacrylic acid is a monomer which is easily transformed to important plastics. Hydrogenation leads to the group of secondary-tertiary glycols, which can be dehydrated stepwise to secondary allyl alcohols and the dienes of the isoprene series; hydrogenation in the presence of ammonia leads to amino alcohols which show some unusual features worthy of further elaboration. The fact that the hydroxyl is tertiary and the amino group primary, causes an obvious difference in their reactivities. In contradistinction to substances like ethanolamine, the amino group will react preferentially—and there are reactions in which this is desirable. On the other hand, dehydration will give an allylamine, and only at a much higher temperature in this vapor phase reaction, will ammonia also be split off—leading again to isoprene and its homologs. Nevertheless, both the tertiary hydroxyl and the primary amino groups participate in the formation of the heterocyclic oxazolidine ring from the amino alcohol and any carbonyl compound.[47] This reaction takes place with surprising ease, and is emulated by that with carbon disulfide or thiophosgene which gives a thiooxazolidone, or rather its tautomeric mercaptooxazoline form.[47] These oxazolidines have an interesting similarity to the imidazolines which have recently found so much attention in therapy[48]; they are more interesting because of the skeleton of isoprene which they contain and which makes them potential analogs, or better isologs, of penicillin. This also contains the (modified) isoprene system, with a thioazolidine instead of an oxazolidine system. Indeed, if one condenses 3-methyl-2-amino-3-butanol with an α-aldehydo-amino acid ester and acylates the amino group, one has a substance which may well be transformable into a close analogon of penicillin:

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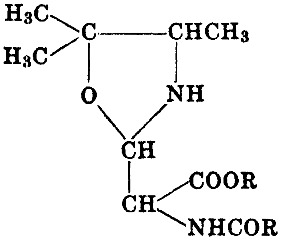
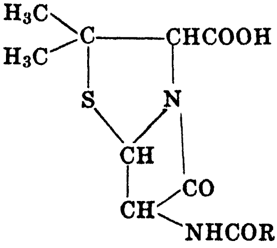
[43] Rupe and Kuenzi, *Helv. Chim. Acta*, 14, 708 (1931). E. Bergmann and F. Bergmann, *J. Am. Chem. Soc.*, 59, 1449 (1937).

[44] See, for example, Hess and Munderloh, *Ber.*, 51, 381 (1918). Scheibler and Fischer, *ibid.*, 55, 2903 (1922). Locquin and Sung, *Compt. rend.*, 176, 516 (1923).

[45] Blumenfeld, U. S. Pat. 2,405,873 (1946); *Chem. Abstracts*, 41, 152 (1947).

[46] Weizmann, Brit. Pat. 569,373 (1944). Unpublished results from our laboratory.





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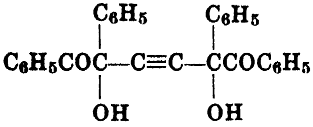
[47] Unpublished results from our laboratory.

[48] Scholz, *Ind. Eng. Chem.*, 37, 120 (1945). Beyer and Morrison, *ibid.*, 37, 143 (1945).

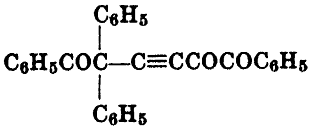
This description of the possible transformations of methylbutynol gains in impressiveness if we remember that an almost unlimited number of homologs and analogs becomes possible if one combines acetylene in the initial reaction with ketones other than acetone, or with aldehydes.

The same is true for the series of tetramethylbutynediol, to which I would like to turn now. Its dehydration leads to a dimethyl-substituted divinylacetylene[49] (again a type of substance which will occupy our attention in the next seminar), but it is accompanied by removal of only one molecule of water. This by-product need not necessarily be a half-dehydration product (a vinylethynylcarbinol). Eckert and Kleinfeller[50] found that the product from two molecules of benzil and bis-bromomagnesylacetylene:



$$C_6H_5CO\overset{C_6H_5}{\underset{OH}{C}}-C\equiv C-\overset{C_6H_5}{\underset{OH}{C}}COC_6H_5$$

rearranges to:



$$C_6H_5CO\overset{C_6H_5}{\underset{C_6H_5}{C}}-C\equiv CCOCOC_6H_5$$

a pinacolinic rearrangement through the interposed acetylenic system.

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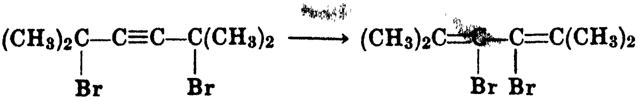
[49] See, for example, Dupont, *Compt. rend.*, 152, 197 (1911); *Ann. chim.*, 30, 512 (1913). Mitchell and Marvel, *J. Am. Chem. Soc.*, 55, 4276 (1933). Butz, Gaddis, Butz, and Davis, *J. Org. Chem.*, 5, 379 (1940).

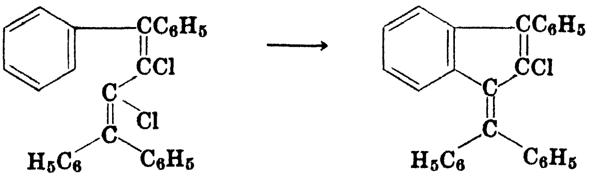
[50] Kleinfeller and Eckert, *Ber.*, 62, 1598 (1929). Eckert, *ibid.*, 72, 249 (1939).

The hydroxyl groups can be acetylated[51] and etherified[52] and replaced by halogen. However, the halides are not stable: the dibromide rearranges spontaneously[53] into 1,1,4,4-tetramethyl-2,3-dibromobutadiene:



$$(CH_3)_2\underset{Br}{C}—C{\equiv}C—\underset{Br}{C}(CH_3)_2 \longrightarrow (CH_3)_2C{=}\underset{Br}{C}—\underset{Br}{C}{=}C(CH_3)_2$$

In the aromatic series, additional types of stabilization have been observed. The acetylenic glycol from benzophenone and acetylene, tetraphenylbutynediol, gives with acetyl chloride 1-benzhydrylidene-2-chloro-3-phenylindene,[54] presumably by the following mechanism:[55]



Equally, with acetyl bromide, a mixture of a colorless dibromo compound[56] and of the corresponding 1-benzhydrylidene-2-bromo-3-phenylindene[57] was obtained, while hydrogen iodide gave the "cumulene" and further the fulvene with the following formulae:[58]

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[51] Dupont, *Ann. chim.*, **30**, 501 (1913). Rupe and co-workers, *Helv. Chim. Acta*, **11**, 449 (1928); **14**, 701 (1931).

[52] Heilbron, Jones, and Weedon, *J. Chem. Soc.*, **1945**, 81. E. Bergmann, *Ber.*, **63**, 2593 (1930).

[53] Krestinsky, *Ber.*, **59**, 1930 (1926). Salkind and co-workers, *Chem. Abstracts*, **22**, 1137, 1586 (1928); **23**, 4678 (1929).

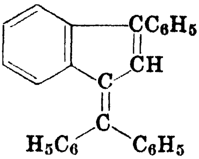
[54] Dupont, *Ann. chim.*, **30**, 493 (1913).

[55] See E. Bergmann and von Christiani, *Ber.*, **63**, 2559 (1930). Wieland and Kloss, *Ann.*, **470**, 201 (1929).

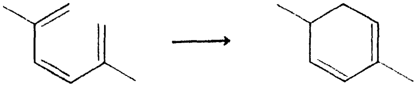
[56] Piganiol, *Bull. soc. chim.*, **9**, 749 (1942).

[57] Unpublished results from this laboratory.

$(C_6H_5)_2C{=}C{=}C{=}C(C_6H_5)_2$



Tetramethylbutynediol can be hydrogenated to tetramethylbutenediol[59] and tetramethylbutanediol.[60] The former can be dehydrated stepwise to tetramethyldihydrofuran[61] and a triene,[62] the latter to tetramethyltetrahydrofuran[63] and, through the corresponding dibromide, to diisopropenylethane.[64] Oxidation of the latter leads to acetonylacetone.[65] It is interesting to observe that the trienes involved have only rarely been obtained in pure form. They isomerize easily, that from tetramethylbutynediol to a dihydro-*p*-xylene:[66]



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[58] Kuhn and Wallenfels, *Ber.*, 71, 783 (1938). Salkind and Krylov, *ibid.*, 61, 2306 (1928); *Chem. Abstracts*, 23, 4678 (1928). Brand, *Ber.*, 54, 2020 (1921).

[59] See, for example, Salkind, *Chem. Abstracts*, 8, 1429 (1914); 18, 2327 (1924); 31, 1012 (1937).

[60] See, for example, Dupont, *Compt. rend.*, 156, 1623 (1913). Kuhn and Wallenfels, *Ber.*, 71, 1889 (1939). I. G. Farbenindustrie, German Pat. 734, 312 (1943); *Chem. Abstracts*, 38, 1250 (1944).

[61] See, for example, Salkind, *Ber.*, 56, 187 (1923); *Chem. Abstracts*, 17, 3477 (1923). Bourguel and Rambaud, *Compt. rend.*, 180, 1753 (1925); 187, 383 (1928); *Bull. soc. chim.*, 45, 1067 (1929); 47, 173 (1930). Johnson and Johnson, *J. Am. Chem. Soc.*, 62, 2615 (1940).

[62] Kuhn and Wallenfels, *Ber.*, 71, 1889 (1939). Burkhardt and Hindley, *J. Chem. Soc.*, 1938, 987. Lozach, *Bull. soc. chim.*, 8, 519 (1941).

[63] Beilstein, Vol. XVII, p. 16.

[64] Harries and Tuerk, *Ann.*, 343, 365 (1905).

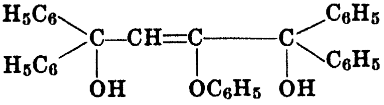
[65] Unpublished results from our laboratory.

[66] Salkind, *Chem. Abstracts*, 17, 3477 (1923).

There is a distinct difference in the rates of these reactions between *cis* and *trans* forms of the ethylenic glycols, which have both been prepared in a number of cases. In order to cyclize, the *trans* isomers have to undergo stereoisomerization. Recently,[67] an indirect method for the preparation of the trienes has been worked out, *viz.*, the conversion of the butenediols to the corresponding chlorides and the dehydrohalogenation of the latter with pyridine.

The triple bond in tetramethylbutynediol can be oxidized, which again gives α-hydroxyisobutyric acid[68] and, therefore, methacrylic acid; it lends itself to the other normal reactions, but the hydration takes an unexpected course. The corresponding dihydroxy ketone is not obtained if one treats the diol with a neutral aqueous solution of mercuric sulfate. The expected product cyclizes to tetramethylketotetrahydrofuran, a substance with a camphorlike odor, an interesting solvent capable of many transformations.[69]

A special case might be mentioned in this connection—the addition of phenol to tetraphenylbutynediol. This leads, if carried out in the presence of sulfanilic acid as a catalyst, according to a recent paper by Salkind,[70] to three main products, the structures of which can be explained in the following way. The phenol adds either as $\mathrm{H{-}OC_6H_5}$ or as $\mathrm{H{-}C_6H_4OH}$; in the former case:



$$\mathrm{(H_5C_6)_2C(OH){-}CH{=}C(OC_6H_5){-}C(OH)(C_6H_5)_2}$$

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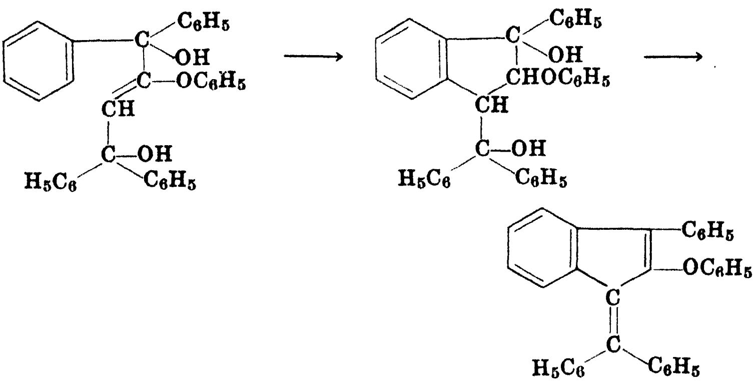
[67] Werner and Reynolds, *J. Am. Chem. Soc.*, **69**, 633 (1947). Compare Valetta, *Compt. rend.*, **223**, 907 (1946).

[68] Lvov, Akopyan, and Polyuta, *Chem. Abstracts*, **35**, 5858 (1941). Dupont, *Compt. rend.*, **150**, 1523 (1910); *Ann. chim.*, **30**, 529 (1913). Krestinsky, *Ber.*, **59**, 1930 (1926).

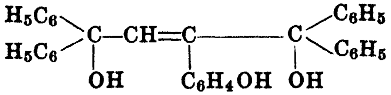
[69] Blomquist and Marvel, *J. Am. Chem. Soc.*, **55**, 1655 (1933). Dupont, *Compt. rend.*, **152**, 1486 (1911); **153**, 275 (1911); *Ann. chim.*, **30**, 535 (1913). Henecka, *Chem. Abstracts*, **31**, 5792 (1937).

[70] Salkind, *Chem. Abstracts*, **40**, 4709 (1946).

is formed, which spontaneously gives the corresponding substituted dihydrofuran or cycloisomerizes as all allylbenzenes do:



Finally, this molecule loses two molecules of water and gives 1-benzhydrylidene-2-phenoxy-3-phenylindene. Equally, the *p*-hydroxyphenyl derivative:



$$(H_5C_6)_2\underset{\displaystyle OH}{\underset{|}{C}}-CH=\underset{\displaystyle C_6H_4OH}{\underset{|}{C}}-\underset{\displaystyle OH}{\underset{|}{C}}(C_6H_5)_2$$

gives 1-benzhydrylidene-2-(*p*-hydroxyphenyl)-3-phenylindene.

Before we go further, let us pause for a while and admire the two schemes we have discussed, that of Reppe and that of Weizmann, based on Favorski's original observation. They supplement each other, if we only look at the cases of formaldehyde, acetaldehyde, and acetone, and make available from acetylene all the monomers which the modern industry of high polymers requires and a large number of new ones which hold out no lesser promise. This is particularly true of the Weizmann scheme. It has the added feature that, while formaldehyde is a substance which is outside the range of acetylene chemistry (this, of course, is not the case for acetaldehyde), acetone and therefore, for example, also methyl isobutylketone, can be made from acetylene only. The reaction is complex. It involves: (*1*) the hydration of acetylene to acetaldehyde, $2\,HC{\equiv}CH + 2\,H_2O \rightarrow 2\,CH_3CHO$; (*2*) its oxidation to acetic acid, $2\,CH_3CHO \rightarrow 2\,CH_3COOH$; and (*3*) ketonization, $2\,CH_3COOH \rightarrow CH_3COCH_3 + CO_2$. Nevertheless, it proceeds in an extremely fast manner and in excellent yield (93%) when acetylene, mixed with steam, is passed at almost 450° over a catalyst such as zinc vanadate.[71]

Acetylene provides us with all the substances required for the production of the known synthetic rubbers—with the exception of isobutylene—especially if we recall that styrene can be made from butadiene through vinylcyclohexene and that acrylonitrile is also easily available from acetylene. We can round off the picture by remembering that vinyl chloride and vinyl acetate are also made from acetylene. And, of course, there are the many new substances and new types of substances which Reppe's vinylation reaction has made so easily accessible: the vinyl alkyl ethers which are best polymerized with boron trifluoride either to highly viscous oils or to rubbers, hard plastics, or brittle resinlike materials. They can be cross linked to insoluble products if one adds in the polymerization traces of divinyl ethers, such as those of the glycols. The other extreme is the polymerized vinyl methyl ether, which is soluble in water below 35° and coagulates reversibly above that temperature. Vinyl ethers also have the surprising property that, if they are copolymerized in small quantities with vinyl chloride, the polymer is very much more soluble in varnish and lacquer solvents than polyvinyl chloride (Vinoflex M.P. 400). Similarly outstanding properties are exhibited by certain vinyl esters. That of tall-oil acid (mixture of linoleic, linolenic, and abietic acids) is a very good substitute for linseed oil in color printing and also as a size in the textile industry.[72]

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[71] Platonow and co-workers, *Chem. Zentr.*, 1935, II, 502; 1941, I, 1738; 1942, II, 2419. Deutsche Gold- und Silber-Scheideanstalt, German Pat. 619,297 (1935).

The most interesting feature of these schemes seems to me to be the fact that isoprene has now become an easily available substance. This will enable the chemist to return to this hydrocarbon on a scale which is commensurate with its importance as *the* building stone of natural rubber, and to leave alone for a while butadiene which, at the time of the rapid development of synthetic rubber, had only the advantage that it appeared to be more easily accessible. But isoprene is not only important to the rubber chemist. For some time now it has been recognized that a large number of natural substances appear to consist of recurrent isoprene units—the carotenoids, many essential oils, the terpenes, even the steroids; and not infrequently a proposed formula in one of these fields has been rejected because it could not be constructed from isoprene units.[73] Of course, one would not conclude that isoprene is actually the building stone of these molecules; I believe that this is not even true for natural rubber. But what is the biogenetic mechanism which produces the isoprene skeleton? It must involve a substance that contains the C atoms in the desirable arrangement and in a form giving them high reactivity, and it must involve a substance which can be formed under biological conditions from normal constituents of living cells.[74] We have encountered such a substance. It is dimethylacrolein. We have mentioned parenthetically that it is capable of self-condensation to the isoprenoid molecules dehydrogeranial and dehydrofarnesal, because of the fact that, through the double bond, the carbonyl group activates the methyl group as much as if it were in its immediate vicinity. The condensation product always retains one active group which can initiate further condensation, and the α,β double bond will make cyclization reactions easy and is sufficiently active for hydrogenation under biological conditions. It is, therefore, very gratifying that a short time ago Kuzin and Nevraeva[75] showed that acetone and acetaldehyde can undergo a mixed aldol reaction which leads to β-hydroxyisovaleraldehyde, a hydrated form of dimethylacrolein. This is surprising as laboratory experience shows that the normal condensation of an aldehyde and acetone will always lead to an alkylideneacetone. It appears, however, that with glycine as catalyst—indeed, a biologically possible system—that rule is reversed.[76] The condensation product showed all the typical reactions of an aldehyde and could be oxidized to the corresponding acid. The dimethylacrolein thus also becomes an interesting starting material for the biochemist in his attempts to emulate nature.

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[72] Swedish Pat. 98,482; Italian Pat. 376,011 (quoted by Reppe, *Advances in Acetylene Chemistry*).

[73] See, for example, Lederer, Mercoer, and Perot, *Bull. soc. chim.*, **1947**, 345.

This brings us to the end of our survey of the reactions of acetylene—with one exception, polymerization, especially to the interesting lower polymers such as vinylacetylene and cyclooctatetraene. Their discussion in the next seminar will give us the possibility of answering some fundamental questions concerning the electronic structure of the acetylene system; these answers will enable us to explain a number of reactions characteristic of much more complex acetylene derivatives which—at least so far—have only been attractive for the theoreticians among the organic chemists.

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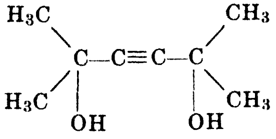
[74] This has already been suggested by Euler and Klussman, *Chem. Zentr.*, 1932, II, 2201. Tobolsky, Castro, Stein, and Sacher [*J. Polymer Sci.*, 2, 246 (1947)] have recently developed the theory that the isoprenoids in nature are decomposition (oxidation) products of a radical chain of polyisoprene.

[75] Kuzin and Nevraeva, *Biokhimiya*, 6, 261 (1941); *Chem. Abstracts*, 35, 7427 (1941).

[76] The catalytic influence of amino acids on the *self-condensation* of dimethylacrolein has been observed by Fischer and Marshall, *Ber.*, 64, 2825 (1931).

THIRD LECTURE

In the last seminar we studied the reactions of the acetylenic carbinols which can be made from acetylene and aldehydes or ketones either by means of copper acetylide or of potassium hydroxide in conjunction with certain solvents. The acetylenic carbinols and the diols like:



$$(H_3C)_2C(OH)-C\equiv C-C(OH)(CH_3)_2$$

give all the normal reactions of substituted acetylenes in addition to those of tertiary alcohols.

The picture would not be complete if we did not elaborate somewhat on the peculiar properties of the system potassium hydroxide plus solvents such as acetal or glycol dialkyl ethers. Undoubtedly, the alkali hydroxide shows some peculiar properties in this system, which can again best be explained by the hypothesis that a molecular compound is formed. With its help one can alkylate with alkyl halides ethyl acetoacetate, ethyl malonate, ethyl cyclopentanone-2-carboxylate, and other doubly activated reactive methylene or methine groups of this type in the same way as it is done with a solution of sodium metal in anhydrous alcohol.[1] The esters are not hydrolyzed (even if the potassium hydroxide used contains water) ; only the alkyl halide is slowly hydrolyzed if its rate of reaction with the reactive methylene or methine group is not high enough. One can alkylate benzyl cyanide and even ethyl phenylacetate and the aliphatically disubstituted acetic acid esters — this last reaction being a somewhat surprising feature. The condensation of indene or fluorene or benzyl cyanide with aldehydes and ketones is catalyzed; so is the Michael condensation between α,β-unsaturated carbonyl compounds or esters and substances containing reactive hydrogen—again a reaction which usually requires alkali alkoxides in absolute alcohols.[2] Not all condensation reactions, however, are catalyzed by this new reagent: ethyl acetate and acetone do not give acetylacetone; ethyl adipate does not give ethyl cyclopentanone-2-carboxylate, but it is characteristic that even prolonged heating at 100°C. does not lead to any saponification of the adipate. An interesting case in which the new reagent has proven rather advantageous is the condensation of acetone and chloroform to trichloro-*tert.* butyl alcohol.[3] This reaction was known: under the best conditions, using potassium hydroxide in ether, it gives about a 25% yield.[4] It is true that sodamide enables one to obtain the chlorinated alcohol in 75% yield,[5] but it requires absolute exclusion of traces of humidity and is certainly not easy to handle. The new reagent gives an 85% yield and permits the condensation of chloroform with other ketones and even with such aldehydes as are not resinified by potassium hydroxide even at low temperatures, *i.e.*, benzaldehydes and α-branched aliphatic aldehydes.[3] I mention "acetone–chloroform" in this connection particularly because it opens an obvious new route to the synthesis of methacrylates. It is the orthochloride of α-hydroxyisobutyric acid, and a look at the three starting materials we now have for this acid shows the parallelism of the processes:

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[1] Weizmann, Brit. Pat. 582,191 (1946) ; *Chem. Abstracts*, 41, 2436 (1947).

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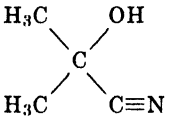
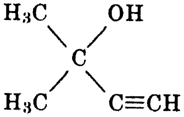
[2] Weizmann, Brit. Pat. 594,182 (1947).

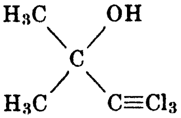
[3] Bergmann and Sulzbacher, Brit. Pat. 587,275 (1947).

[4] See Fishburn and Watson, *J. Am. Pharm. Assoc.*, 28, 491 (1939).

[5] Schwyzer, *Fabrikation pharmazeutischer und chemisch-technischer Produkte*, Springer, Berlin, 1931, p. 112. See also Wiernick, German Pat. 515,539 (1931); *Chem. Zentr.*, 1931, I, 2394.







Indeed, all three can be converted into methacrylates; this is not the place to elaborate upon the best way to be used in the case of the halogenated alcohol.[6] But I would like to point out that the above-mentioned possibility of condensing chloroform with other carbonyl compounds makes available a whole series of homologs and analogs of methacrylic acid.

We have now to turn to one last point in the discussion of the reactions of acetylene: its polymerization. Until a few years ago almost no well-defined polymerization of acetylene was known. The only, at least industrially, defined acetylene polymer was cuprene.[7] Of all the metals, copper alone converts acetylene into a voluminous, fiberlike solid, which has been used as a cork substitute and a safety carrier for inflammable and explosive liquids. Copper oxide has the same effect, obviously because of its reduction to the metal for which the decomposition of the acetylene supplies the hydrogen. The temperature is limited to 180–250°C.; below 180° mostly liquid polymers are formed, of which we will speak presently; above 250° excessive decomposition into carbon and hydrogen takes place, the carbon in turn catalyzing the formation of liquid aromatic and olefinic hydro-

[6] Weizmann, Brit. Pats. 578,082 (1946), 584,607 (1947); *Chem. Abstracts*, 41, 2075, 3812 (1947).

[7] Sabatier and Senderens, *Compt. rend.*, 128, 1173 (1899); 130, 250, 1559 (1900); 131, 187 (1900).

carbons. The composition of cuprene is approximately (C_7H_6); the copper which is usually found in crude samples can be removed by treatment with ferric chloride solution in hydrochloric acid. Cuprene is of an aromatic nature, since concentrated nitric acid converts it into mellitic acid.

Kinetic investigation[8] of cuprene formation leads to the belief that it is a real polymerization, with an exothermicity of 61–70 kcal. per mole of acetylene. The reaction shows a definite induction period and requires some oxygen to start with. It is not possible that an aromatic ring is formed in one step from 3 moles C_2H_2—though this is a generally accepted belief—either in the formation of cuprene or in the classical polymerization of acetylene to benzene and it will be necessary to study in somewhat greater detail that reaction which, generally speaking, occurs in the high-temperature treatment of acetylene. Benzene is formed, for example, from acetylene in one of the typical Berthelot experiments, when it is passed through a retort heated to the softening point of the glass.[9] The yield improves if the high-temperature treatment is carried out at 645–800° (in two steps) in the presence of hydrogen, which suppresses the decomposition of the acetylene into the elements.[10] But even so, it is not true that benzene is *the* product of the reaction. One obtains, as far as the liquid condensate is concerned: benzene (20% of the liquid), a trace of toluene and the xylenes, a 150–200° cut, containing indene, a 200–300° cut, containing naphthalene, diphenyl, fluorene, and a trace of methylnaphthalenes, and further some pyrene and chrysene. Equally, a mixture of aromatics is obtained when acetylene is brought into contact with molten salts.[11]

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[8] Calhoun, *Can. J. Research,* B15, 208 (1937). Kaufmann and Monhaupt, *Ber.,* 56, 2533 (1923).

[9] Berthelot, *Bull. soc. chim.,* 6, 268 (1866); *Compt. rend.,* 62, 905 (1866).

[10] Meyer and co-workers, *Ber.,* 45, 1609 (1912); 46, 3183 (1913); 47, 2765 (1914); 51, 1571 (1918); 53, 1261 (1920); 55, 819 (1922).

This, of course, is a quite different picture which recalls the composition of the aromatic product formed by high-temperature cracking of mineral oils. In this latter reaction, it has been shown that the central part in the reaction scheme is played by butadiene, a C_4 compound[12]; and it is reasonable to assume that acetylene is also first converted into a C_4 compound, which then reacts further to give the products actually found. Before we try to show that such a reaction is possible, I would like to mention as an illustration the fact that if the thermal treatment mentioned is applied to a mixture of acetylene and ethylene, butynes and butadienes are formed, in however low a yield,[13] and that a mixture of acetylene and benzene appears to give styrene and its polymers under these conditions.[14]

It is worth mentioning that a much better process for the "liquefaction of acetylene" and especially its conversion into benzene has recently been found.[15] If acetylene is passed over aluminum carbide at 720° with a contact time of 30 to 100 seconds, 90% is converted into an oil. This consists of 50–60% benzene, 10–15% toluene, ethylbenzene, xylene, styrene, 10–15% naphthalene, 5–10% biphenyl, and 5–10% anthracene.

The dimerization reaction of acetylene to which I referred was discovered by Nieuwland.[16] If one passes acetylene at 65° at a very high speed through an acid solution of cuprous and ammonium chloride, substantial amounts of a hydrocarbon C_4H_4 are formed. It is necessary to maintain a *p*H of about 1.5 so as to avoid the formation of copper acetylide. If one leaves the acetylene in the catalyst solution (which absorbs it readily) for 7 days, 70% of it is converted into a hydrocarbon C_6H_6, an interesting isomer of benzene. It has been proven that the two hydrocarbons are vinylacetylene and divinylacetylene:

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[11] Johnson and Swann, *Ind. Eng. Chem.*, 38, 990 (1946).

[12] Weizmann, Bergmann, Steiner, and Sulzbacher, paper read before the Congress of Pure and Applied Chemistry, Paris, 1946.

[13] Plauson and Vieille, Brit. Pat. 156,116 (1921).

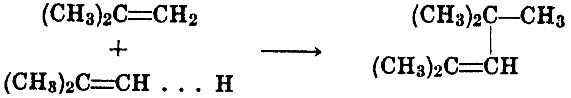
[14] Varet and Vienne, *Compt. rend.*, **164**, 1375 (1886). See, however, Cook and Chambers, *J. Am. Chem. Soc.*, 45, 334 (1923), and Boeseken and Adler, *Rec. trav. chim.*, 48, 474 (1929).

[15] Pascal and Coupard, *Compt. rend.*, 214, 757 (1942).

[16] Nieuwland and co-workers, *Science*, 56, 486 (1922); *J. Am. Chem. Soc.*, 53, 4197 (1931); U. S. Pats. 1,811,959; 1,812,541; 1,812,849; 1,812,544 (1931); U. S. Pat. 1,869,668 (1932). Mita, *Chem. Abstracts*, 41, 3038 (1947).

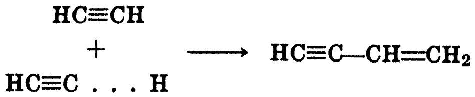
$H_2C{=}CH{-}C{\equiv}CH$ and $H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$

What is the mechanism of their formation? It is the normal one by which olefins also are dimerized and which can be described in general terms by saying that one CH bond adds as C—H to the unsaturated C=C bond in a second molecule. In the olefinic series there is always a tendency to convert a terminal methylene to a methyl group,[17] for example:



$$\begin{array}{c}(CH_3)_2C{=}CH_2\\ +\\ (CH_3)_2C{=}CH\ldots H\end{array}\longrightarrow\begin{array}{c}(CH_3)_2C{-}CH_3\\ |\\ (CH_3)_2C{=}CH\end{array}$$

The same happens here:



$$\begin{array}{c}HC{\equiv}CH\\ +\\ HC{\equiv}C\ldots H\end{array}\longrightarrow HC{\equiv}C{-}CH{=}CH_2$$

In the further reaction of vinylacetylene, which leads to higher polymers of acetylene, a large number of alternative possibilities are given by this simple scheme. Any one of the three CH groups present can react; each one of them can react with acetylene or with vinylacetylene—in the latter case, each of them can add either to the double bond or the triple bond or in 1,4 position, and one may even have to envisage the possibility that two directions are open in each case for the addition. In the formation of divinylacetylene, obviously the terminal CH group of vinylacetylene adds to acetylene in the normal way. But the crude reaction product contains more than only vinyl- and divinylacetylene. Three additional substances were identified as follows: $CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH{-}C{\equiv}CH_2$, 1,5,7-octatrien-3-yne; $CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}C{\equiv}CH$, 1,3,5-octatrien-7-yne; and $CH_2{=}CH{-}CH{=}CH{-}CH{\equiv}CH$, 1,3-hexadien-5-yne. The last one, an isomer of divinylacetylene, is formed from vinylacetylene and acetylene either by addition of the terminal methylene group to acetylene:

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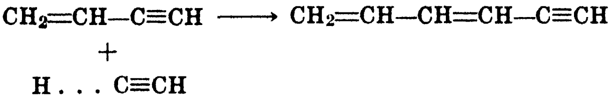
[17] See E. Bergmann, *Trans. Faraday Soc.*, 35, 1025 (1939).

$$CH{\equiv}C{-}CH{=}CH\ldots H + HC{\equiv}CH \rightarrow CH{\equiv}C{-}CH{=}CH{-}CH{=}CH_2$$

or by addition of acetylene to the acetylenic bond of vinylacetylene:



$$\begin{array}{l} CH_2{=}CH{-}C{\equiv}CH \longrightarrow CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH \\ \qquad + \\ H\ldots C{\equiv}CH \end{array}$$

I prefer the first mechanism for reasons of analogy.

In order to formulate the formation of the two C_8 hydrocarbons, it is important to know that the first is obtained, together with higher, insoluble polymers, when vinylacetylene is kept in contact with cuprous chloride.[18] It owes its existence, therefore, to the addition of one molecule, acting with its acetylenic, terminal CH group, to the acetylenic bond of a second molecule:

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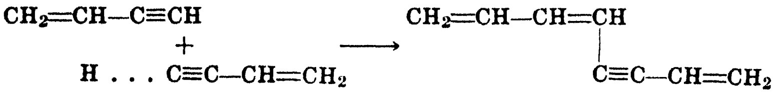
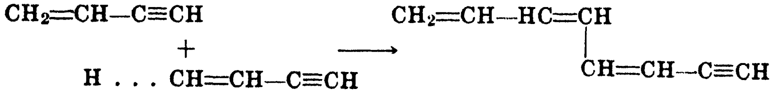
[18] Nieuwland, Calcott, Downing, and Carter, *J. Am. Chem. Soc.*, 53, 4197 (1931). Dykstra, *ibid.*, 56, 1625 (1934). Rotenberg and Favorskaya, *Chem. Abstracts*, 30, 4808 (1936).



$$\begin{array}{l} \mathrm{CH_2{=}CH{-}C{\equiv}CH} \\ \qquad\qquad + \\ \mathrm{H\ .\ .\ .\ C{\equiv}C{-}CH{=}CH_2} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_2{=}CH{-}CH{=}CH} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad \mathrm{C{\equiv}C{-}CH{=}CH_2} \end{array}$$

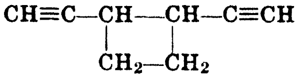
and that is the reason why we rejected the second formulation for the reaction of vinylacetylene with a further acetylene molecule.

As to the other octatrienyne, it is formed analogously, the other terminal CH group being the addition agent:



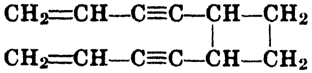
$$\begin{array}{l} \mathrm{CH_2{=}CH{-}C{\equiv}CH} \\ \qquad\qquad + \\ \mathrm{H\ .\ .\ .\ CH{=}CH{-}C{\equiv}CH} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_2{=}CH{-}HC{=}CH} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad \mathrm{CH{=}CH{-}C{\equiv}CH} \end{array}$$

All these hydrocarbons are extremely reactive. They absorb oxygen with great avidity giving peroxides which explode violently on heating or when subjected to shock. They also polymerize further with great ease and give products, partly low- and partly high-molecular, which are only insufficiently known as far as their structure is concerned. The product obtained from vinylacetylene by heat dimerization, *e.g.*, (in the absence of air) has been formulated as a cyclobutane:[18]



$$\begin{array}{l} \mathrm{CH{\equiv}C{-}CH{-}CH{-}C{\equiv}CH} \\ \qquad\quad\ |\qquad\ | \\ \qquad\quad \mathrm{CH_2{-}CH_2} \end{array}$$

and analogously that from divinylacetylene assumed as:[19]



$$\begin{array}{l} \mathrm{CH_2{=}CH{-}C{\equiv}C{-}CH{-}CH_2} \\ \qquad\qquad\qquad\quad\ |\qquad | \\ \mathrm{CH_2{=}CH{-}C{\equiv}C{-}CH{-}CH_2} \end{array}$$

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[19] Cupery and Carothers, *J. Am. Chem. Soc.*, 56, 1167 (1934); Dykstra, *ibid.*, 56, 1625 (1934).

Now, such formulas are extremely unlikely especially if one considers that the catalytic dimerization of simple olefins has never led to such products, and that the only case in which a cyclobutane derivative is formed is in photodimerization, *e.g.*, of cinnamic acid to truxinic and truxillic acids.[17] Therefore, this is still a problem which awaits solution, and the only positive thing one can say is that the polymers of both mono- and divinylacetylene, if they are not too high molecular, are good drying oils because of the ability of their oxidation products to form films.

There is only one important well-defined polymerization reaction of vinylacetylene, which occurs when it is heated at 105° for 6 hours with dilute (1–10%) acid; it gives styrene and polystyrenes.[20] Similarly, 1-methyl-3-isopropenylbenzene is formed from isopropenylacetylene, and 1,2-dimethyl-4-isopropenylbenzene from 3-methyl-2-penten-4-yne.[21] I believe that one can only explain this as a Diels-Alder reaction, analogous to the formation of vinylcyclohexene from two molecules of butadiene, and it is theoretically interesting to realize that the triple bond resembles a double bond as a philodienic component and as being capable of conjugation with a double bond—a point to which we will return presently. The reaction is not only interesting as a means of producing styrene from acetylene, but also because it shows us how benzene and the other aromatics are most probably formed at high temperatures. Acetylene dimerizes to vinylacetylene, and the latter condenses with acetylene to benzene in exactly the same manner as butadiene condenses with ethylene to cyclohexene.

On the basis of these considerations, we will understand that the chemical reactions of vinyl- and divinylacetylene are the normal reactions for such ethylene and acetylene derivatives, with the qualification that they exhibit the properties of conjugated systems. If, for example, vinylacetylene reacts with hydrochloric acid in the presence of cuprous chloride and ammonium chloride to give chloroprene, one could easily understand that as normal addition to the triple bond—which indeed can be expected to be more reactive (and the same applies to the homologs of the hydrocarbon which, as we saw in the last seminar, are now becoming easily available). However, the reaction is more complex.[22] It begins with a 1,4 addition:

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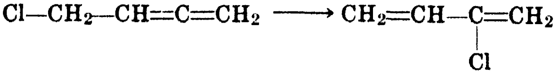
[20] Dykstra, *J. Am. Chem. Soc.*, 56, 1625 (1934). Rotenberg and Favorskaya, *Chem. Abstracts*, 30, 4808 (1930).

[21] Favorskaya and Zacharova, *Chem. Abstracts*, 31, 5318 (1937). Zacharova and Bezel-Sycheva, *ibid.*, 35, 5457 (1941).

$$CH_2{=}CH{-}C{\equiv}CH + HCl \longrightarrow Cl{-}CH_2{-}CH{=}C{=}CH_2$$

The product rearranges, and in this rearrangement the cuprous salt catalyst is necessary:



$$Cl{-}CH_2{-}CH{=}C{=}CH_2 \longrightarrow CH_2{=}CH{-}\underset{\substack{|\\ Cl}}{C}{=}CH_2$$

One will, therefore, assume that all the reactions of vinylacetylene with compounds HX which formally lead to addition at the triple bond may well proceed through the same mechanism, as, for example, the addition of organic acids to give 2-acyloxybutadienes.[23]

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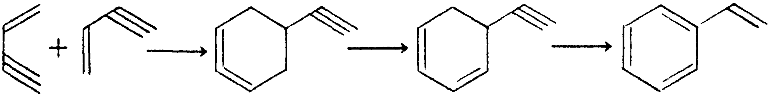
[22] Carothers, Berchet, and Collins, *J. Am. Chem. Soc.*, 54, 4066 (1932). Favorski, *Chem. Zentr.*, **1934, I,** 2488. Sargent and coworkers, *J. Am. Chem. Soc.*, **64,** 2692 (1942). Backer and Blaas, *Rec. trav. chim.*, **62,** 785 (1942).

[23] Werntz, *J. Am. Chem. Soc.*, 57, 204 (1935); U. S. Pat. 1,963,108 (1934); *Chem. Zentr.*, **1936, I,** 2439. Klebanski and Chevuichalova, *Chem. Abstracts*, **29,** 6799 (1935). I. G. Farbenindustrie, French Pat. 869,872 (1942); *Chem. Zentr.*, **1942, II,** 460. For the addition of hydrocyanic acid (cyanoprene), see Kurtz and Schwartz, U. S. Pat. 2,322,696 (1944); *Chem. Abstracts*, **38,** 118 (1944); for that of thiocyanic acid, see Kotake, Mita, and Mikami, *Chem. Abstracts*, **37,** 4055 (1943). The reaction of alcohols with divinylacetylene has been studied by Klebanskii *et al.*, *ibid.*, 41, 3042 (1947).

Of course, vinyl-acetylene is capable of the typical reactions of the terminal acetylenic systems. Its hydrogen can be replaced by metals, and it can be condensed with aldehydes and ketones, either by means of potassium hydroxide or through the bromomagnesyl derivative.[24] It is likely—although it has not yet been tried—that copper can also be used as a catalyst. The vinylethynylcarbinols so obtained have been very thoroughly studied by a number of Russian chemists and by Heilbron and his school in England. Their hydroxyl group is still more peculiar than that of methylbutynol. It has almost the character of the hydroxyl group in triarylcarbinols, *e.g.*, it gives ethers with alcohols and glycols when heated at 60–70° in the presence of a trace of sulfuric acid.[25] The carbinol group plus the neighboring triple bond activate the double bond sufficiently to make it participate in Diels-Alder reactions with dienes. We have seen that methylbutynol does this with the triple bond, but here only the double bond reacts, and it is quite possible to assume that in the dimerization, too, which we have seen to lead to styrene, the mechanism is somewhat more complicated, involving the double and not the triple bond:



The hydroxyl group can undergo anionotropic rearrangement,[26] exactly as in the isomerization of methylbutynol to dimethylacrolein:

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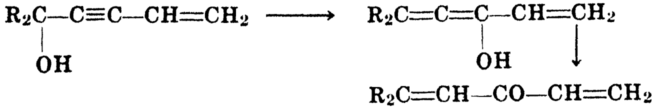
[24] Nazarov and co-workers, *Chem. Zentr.*, **1940, II**, 3554; *Chem. Abstracts*, **38**, 4595 (1944). Carothers and Berchet, *J. Am. Chem. Soc.*, **55**, 1094 (1933).

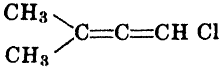
[25] Nazarov, *Chem. Abstracts*, **33**, 5683 (1939); *Chem. Zentr.*, **1940, I**, 3554.



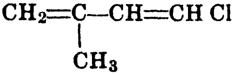
$$R_2C(OH){-}C{\equiv}C{-}CH{=}CH_2 \longrightarrow R_2C{=}C{=}C(OH){-}CH{=}CH_2 \downarrow R_2C{=}CH{-}CO{-}CH{=}CH_2$$

leading to divinyl ketones, which are obviously very prone to polymerization. The same, by the way, is true for the vinylethynylcarbinols themselves which can be converted into technically interesting permanent adhesives.[27]

Equally, the tertiary chlorides corresponding to these vinylacetylenic alcohols can isomerize. This has been known in the series of methylbutynol, where the primary product would be:



as the reaction with silver acetate evidences (see page 13). However, this product rearranges further by a prototropic mechanism, migration of hydrogen, to 1-chloro-3-methyl-1,3-butadiene:[28]



$$CH_2{=}C(CH_3){-}CH{=}CH\,Cl$$

Starting from (methovinylethynyl) dimethylcarbinol, both products can be isolated (see formula I, following page).[29]

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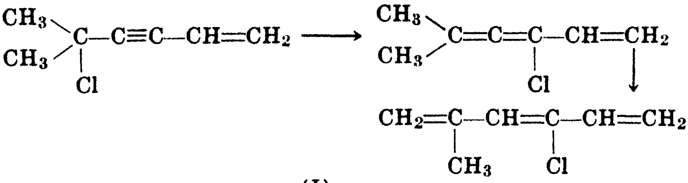
[26] Nazarov, *Chem. Abstracts*, 35, 3593, 4731, 4732 (1941). Nazarov and Okolskaya, *ibid.*, 37, 5369 (1943).

[27] See, for example, Nazarov, *Chem. Abstracts*, 33, 5682 (1939).

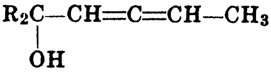
[28] Jacobs and Whitcher, *J. Am. Chem. Soc.*, 64, 2635 (1942).

[29] Nazarov and Yanbikov, *Chem. Abstracts*, 37, 2344 (1943); 38, 1729, 4595 (1944).

The hydrogenation of the vinylacetylenic carbinols also shows the characteristic peculiarities of the acetylenic system with all the complications introduced by the conjugation. The copper-zinc couple attacks the triple bond, converting it into a double bond, but simultaneously the allene is formed by 1,4 addition:[30]

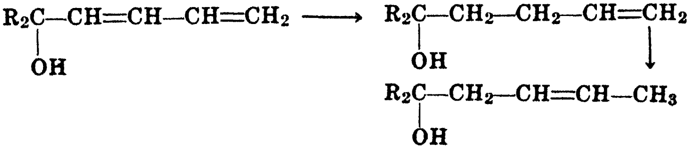


(I)



$$\underset{\displaystyle OH}{R_2\overset{}{C}}—CH{=}C{=}CH—CH_3$$

Palladium causes the addition of four atoms of hydrogen, without break in the rate of hydrogenation, undoubtedly in the following manner—implying first addition at the triple bond only:[31]



$$\underset{\displaystyle OH}{R_2C}—CH{=}CH—CH{=}CH_2 \longrightarrow \underset{\displaystyle OH}{R_2C}—CH_2—CH_2—CH{=}CH_2 \downarrow \underset{\displaystyle OH}{R_2C}—CH_2—CH{=}CH—CH_3$$

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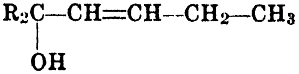
[30] Nazarov and Fischer, *Chem. Abstracts*, 39, 1621 (1945). See also Golovtschanskaya, *ibid.*, 34, 1847 (1940).

[31] Salkind and Chudelova, *Chem. Abstracts*, 34, 7847 (1940). Zonis, *ibid.*, 34, 4052 (1940). Salkind and co-workers, *Chem. Zentr.*, 1936, I, 4161; 1938, II, 768. Thompson, Milas, and Roono, *J. Am. Chem. Soc.*, 63, 752 (1941). Nazarov and Fischer, *Chem. Abstracts*, 38, 4596 (1944).

Nickel behaves in the same way, but gives in addition a third isomer containing one double bond:



$$R_2C(OH){-}CH{=}CH{-}CH_2{-}CH_3$$

and one will have to assume that in this particular instance the intermediate stage is the allenic alcohol.[32]

Let us pause here for a minute and discuss some theoretical conclusions which these facts imply. It is obvious from the behavior of these vinylacetylenic alcohols, from the mode of reaction of the vinylacetylenes with hydrochloric acid, and from the dimerization of vinylacetylene to styrene, that the triple bond can participate in a conjugated system with a double bond; in other words it has electrons, which are free and mobile enough to cause resonance phenomena. We have suspected this from the abnormal electric moments of phenylacetylene and phenylchloroacetylene, but the accumulated material gives a firmer basis to the assumption that the triple bond is a variant of the olefinic double bond. One safe criterion is always the molecular refraction, which shows exaltations for conjugated systems. The divinylacetylenes investigated by Nazarov and the vinylethynylcarbinols show a distinct exaltation of that kind. Another instance is given by the comparison of $CH_3CHOHCH{=}CH{-}C{\equiv}CH$ and the isomer $CH_3CH{=}CHCHOHC{\equiv}CH$ which latter results from the interaction of the pair: acetylenemagnesium bromide and crotonaldehyde, and similar pairs. The former isomer has a much higher refractive index than the latter in which the triple and the double bond are not in immediate vicinity to each other.[33] Another criterion is the absorption spectrum, and here we can quote the following convincing facts. The previously mentioned 3-hexene-1-yne-5-ol has an absorption maximum at 2230 Å, and therefore in a region in which the corresponding diene would absorb. However, the intensity is much lower for the enyne compound (13,500 instead of 23,000), which means that the electrons in the acetylenic bond are less mobile than in the double bond—a fact to which we drew attention in our first seminar.[34] It is equally significant that the extinction coefficient of a diacetylene derivative such as 2,7-dimethylocta-3,5-diyne-2,7-diol is very low:[33]

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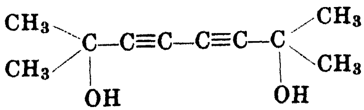
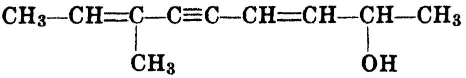
[32] Nazarov and Fischer, *Chem. Abstracts*, 38, 4596 (1944).

[33] Jones and McCombie, *J. Chem. Soc.*, 1943, 261.



and that the divinylacetylenes have considerably smaller extinction coefficients than the corresponding trienes.[35] Furthermore, a substance like:



$$CH_3{-}CH{=}\underset{\displaystyle CH_3}{C}{-}C{\equiv}C{-}CH{=}CH{-}\underset{\displaystyle OH}{CH}{-}CH_3$$

the 3-methylnona-2,6-diene-4-yne-8-ol, has an ultraviolet absorption which lies at the same wave length as that of a triene of the same structure, but again the intensity is reduced (16,500 as against 53,000).[34] The same applies to the α,β-acetylenic ketones such as R—CO—C≡CH in comparison with the analogous vinyl ketones; these acetylenic ketones can be prepared—and that is interesting in itself—

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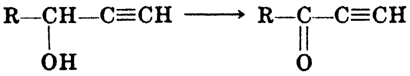
[34] Heilbron, Jones, and co-workers, *J. Chem. Soc.*, **1943**, 261, 264, 265; **1944**, 134, 140, 141, 144. See also Ingold, *Chem. Revs.*, 15, 239 (1934).

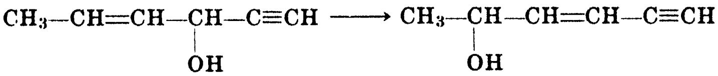
[35] Bastron, Davis, and Butz, *J. Am. Chem. Soc.*, 65, 973 (1943).

by oxidation of the corresponding secondary alcohols with chromic acid:[36]



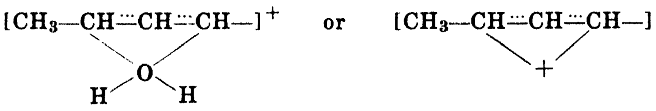
$$R\text{—}\underset{\displaystyle OH}{\underset{|}{C}H}\text{—}C{\equiv}CH \longrightarrow R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}C{\equiv}CH$$

It is undoubtedly the same phenomenon which expresses itself in the following fact.[37] Ethinyl-substituted allyl alcohols can rearrange according to the scheme:



$$CH_3\text{—}CH{=}CH\text{—}\underset{\displaystyle OH}{\underset{|}{C}H}\text{—}C{\equiv}CH \longrightarrow CH_3\text{—}\underset{\displaystyle OH}{\underset{|}{C}H}\text{—}CH{=}CH\text{—}C{\equiv}CH$$

This can be explained by the ability of the ethylenic system to form a transition state:



with the hydrogen ions of the acid medium, while the acetylenic system of the molecule in spite of its analogous position does not participate competitively in the reaction. If one compares analogously built allyl and ethinyl alcohols—which, of course, lead to carbonyl compounds—one finds that the rate of isomerization is 200 to 10,000 times higher for the acetylene than for the olefin derivative. The acetylenic system has four electrons available and, therefore, attracts the positive charge to a lesser extent than the olefinic double bond immediately adjacent to the ionizing atom.

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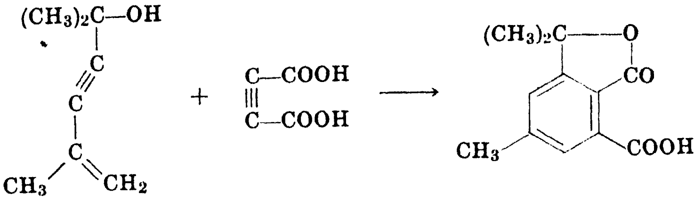
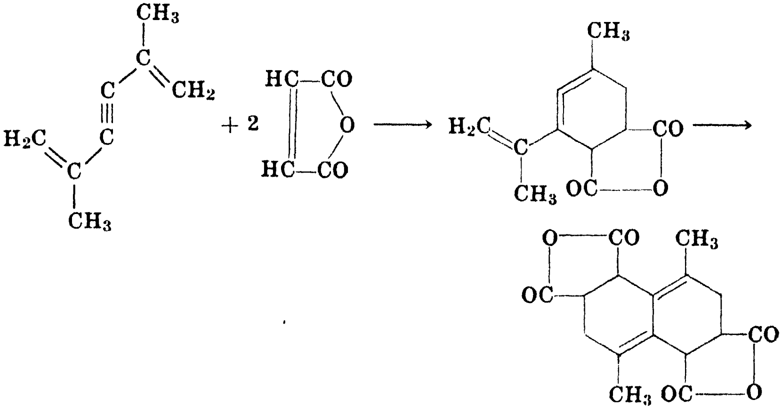
[36] Bowden, Heilbron, Jones, and Weedon, *J. Chem. Soc.*, 1946, 39.

[37] Cymerman, Heilbron, and Jones, *J. Chem. Soc.*, 1945, 90. Heilbron, Jones, McCombie, and Weedon, *ibid.*, 1945, 84. Braude and Jones, *ibid.*, 1944, 436. Braude, *ibid.*, 1944, 443.

As already indicated briefly, the conjugation between double and triple bonds in such systems is also evident from the addition reactions which these substances enter into with philodienic components, even including ethylene.[38] The half-dehydration product of tetramethylbutynediol, for example, gives with propiolic acid the following aromatic lactonecarboxylic acid:[39]



and substituted divinylacetylenes are even capable of reacting with two molecules of the philodienic component:[40]



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[38] Butz and Joshel, *J. Am. Chem. Soc.*, **63**, 3350 (1941).

[39] Johnson, *J. Chem. Soc.*, **1945**, 715. Dane and co-workers, *Ann.*, **532**, 43 (1937); **536**, 183 (1938).

[40] Butz and co-workers, *J. Am. Chem. Soc.*, **62**, 995 (1940); **63**, 3344, 3348, 3350 (1941); **64**, 1311 (1942); **65**, 2059 (1943); *J. Org. Chem.*, **5**, 379 (1940); **7**, 199 (1942). Dane, Hoss, Eder, Schmitt, and Schoen, *Ann.*, **536**, 183 (1938).

These facts and speculations provide us with a good tool in the discussion of one of the most surprising polymerization reactions known—that of four molecules of acetylene to cyclooctatetraene—which has been developed in Germany on an industrial, or at least semi-industrial, scale.[41] It takes place when acetylene under pressure is brought into contact with nickel halides or cyanide in tetrahydrofuran containing a small amount of ethylene oxide as solvent. These conditions are somewhat reminiscent of alchemy, especially as the role of the various ingredients has not become clear from the reports so far available. It is not clear whether tetrahydrofuran is merely a good solvent for acetylene or whether it is essential in the mechanism of the process. It is not clear whether ethylene oxide serves to dry the tetrahydrofuran, which, boiling at 65°C., it is difficult to dehydrate completely, or whether it constitutes—together with the nickel compounds—the catalytic agent. It is probable that the nickel halides give transient acetylene nickel compounds which are more reactive than acetylene itself, and Reppe presumes that the nickel halides react with ethylene oxide to form nickel derivatives of the halogeno-ethyl alcohols, which are supposed to react more easily with acetylene than the inorganic nickel salts themselves. However this may be, one thing will be clear to us at once: the reaction cannot be a simple one-step tetramerization of the acetylene. This is not only excluded by the laws of probability, but would also fail to explain why the molecule does not prefer to trimerize rather than to tetramerize. Unquestionably, benzene is thermodynamically more favored. One can see that by merely comparing the heats of formation:

$$3\,C_2H_2 = C_6H_6 + 147\ \text{kcal.}$$

$$4\,C_2H_2 = C_8H_8 + 180\ \text{kcal.}$$

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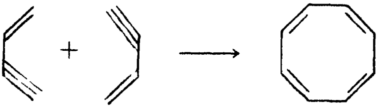
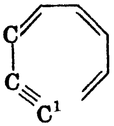
[41] British Intelligence Objectives Sub-committee, Final Report No. 137 and Appendix, Item No. 22.

As one knows from the classical papers of Willstätter,[42] who has first prepared the hydrocarbon by an elegant, but devious route, cyclooctatetraene is by no means as saturated as benzene; a more detailed discussion of the properties of cyclooctatetraene, which we will give presently, confirms this impression. How then is it possible to explain its easy formation? I believe that the first reaction—as in presence of copper salts which share the electronic configuration of the metal ion with nickel salts—is a dimerization to vinylacetylene, and that this dimerizes to give the cyclic compound:



I would go further and assume that the dimerization does not lead directly to the cyclooctatetraene, but rather to one of the open-chain C_8H_8 compounds we have already encountered:



The C^1 atom is kept on the nickel surface in the form of a nickel complex and the other terminal group is, therefore, capable of reacting preferentially. Finally, a cycloisomerization of a common type takes place, which requires that the chain be in the correct configuration, *i.e.*, that the two inner double bonds have a *cis* structure. This, undoubtedly, gives a good mechanical picture of the situation, but it is not sufficiently confirmed experimentally to exclude another possibility which arises from the following facts. Before the reports from Germany were available, substituted cyclooctatetraenes[43] were successfully synthetized, which, incidentally, gave the first indication that this ring system is not like that of benzene. The bimolecular dehalogenation of *o,o′*-dibromobiphenyl gave the so-called tetraphenylene—tetrabenzocyclooctatetraene—and although it showed physical properties which could only be understood if one assumed that the ring system was not planar, and therefore lacked the most essential prerequisite of the benzene nucleus, it showed certain remarkable features. Oxidation, for example, converted one of the 6-membered rings to a dicarboxylic acid:

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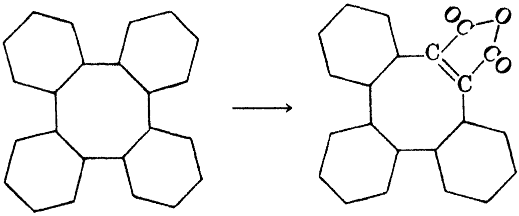
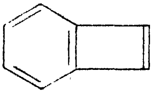
[42] Willstätter and co-workers, *Ber.*, 44, 3442 (1911); 48, 5518 (1915).



which could be decarboxylated to tribenzocyclooctatetraene. This series of reactions does not give us any clue as to the mechanism of formation of the parent substance; but it stirred up interest in a hydrocarbon which may very well be a dibenzocyclooctatraene.[44] This hydrocarbon is formed when tetrabromo-*o*-xylene is dehalogenated, *e.g.*, with sodium iodide. One might expect a product of the formula:



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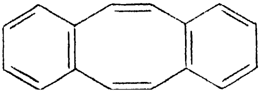
[43] Rapson and co-workers, *J. Chem. Soc.*, 1943, 326; 1944, 71, 73. See also Fieser and Pechet, *J. Am. Chem. Soc.*, 68, 2577 (1946).

[44] Unpublished results from our laboratory.

a cyclobutadiene derivative, but this is unlikely for reasons of steric strain and, moreover, it proved to be dimolecular. Would it not be feasible to assume that it is dibenzocyclooctatetraene:



and that the formation of the parent substance from acetylene proceeds analogously through dimerization of cyclobutadiene itself? This remains to be seen, and it remains above all to carry out the corollary experiments which are suggested by our first—and, I believe, more plausible—mechanism. One would expect that the octatrienyne with a terminal acetylene bond can be converted into cyclooctatetraene and that this hydrocarbon is also formed from vinylacetylene under the above-defined reaction conditions. One would further expect methylation of the terminal acetylenic carbon atom to at least reduce the cycloisomerization rate because of the lower affinity of the methylated product for nickel. It appears also possible that an octatetraene can be dehydrogenated to cyclooctatetraene, provided that the double bonds are in the correct position—and very probably, such *cis-cis*-octatetraenes can be easily prepared from the diacetylenic glycols we discussed in the last seminar, by half-hydrogenation of the triple bonds and subsequent dehydration.

It is also characteristic in this respect that the formation of cyclooctatetraene is accompanied by that of higher homologs which, however, have not yet been isolated in pure form or identified in a proper manner. One is said to be the cyclodecapentaene, which would result from the combination of vinylacetylene and a divinylacetylene with a terminal triple bond—a substance which we have encountered as a by-product of the cuprous salt-catalyzed polymerization of acetylene. Here, too, a number of new experimental possibilities suggest themselves. Another homolog which has been provisionally identified is the cyclohexadodecaene. The best temperature for the preparation of C_8H_8 is 50–60°; $C_{10}H_{10}$, 90–100°; and $C_{12}H_{12}$, 130–140°. Certain chemical reactions speak definitely against the suggested structures (although, as we will see, rearrangements in this group are normal even in simple reactions) : the hydrogenated $C_{10}H_{10}$ is not identical with cyclodecane and gives, upon oxidation, only suberic acid; the hydrogenated $C_{12}H_{12}$ gives, upon dehydrogenation, 1,2-dimethylnaphthalene.

But let us return to cyclooctatetraene, which, as we said before, is not similar to benzene—or at least it does not fully approximate benzene in its properties and behavior. It is rather an intermediate between an open-chain tetraene and a cyclic compound of benzene type.

The structure of the molecule is certainly symmetrical. This is best shown by the Raman spectrum which consists of 7 instead of the possible maximum 42 lines. But the wave lengths of the lines corresponding to the C—C and the C—H linkages are not identical with those of benzene: 1673 and 3068 instead of 1605 and 3060. A recent closer investigation[45] has shown that the symmetry is not that of a planar molecule with an eightfold axis (the number of polarized lines is too large for that) or of a molecule with cubic symmetry; but one can definitely conclude that all hydrogen atoms are equivalent and that the molecule exhibits a multiple axis of symmetry. The best explanation[45a] is a puckered structure, similar to, but more outspoken than, cyclohexane.

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[45] Lippincott and Lord, *J. Am. Chem. Soc.*, 68, 1868 (1946). For the infrared and Raman spectra of cyclooctatetraene, see also Flett *et al.*, *Nature,* 159, 739 (1946) ; Hassel *et al.*, *ibid.*, **160**, 128 (1947).

[45a] The electron diffraction has been studied by Bastiansen, Hassel, and Langseth, *Nature,* **160**, 128 (1947).

The same conclusion can be reached from the heat of combustion.[46] If one calculates from it the energy of resonance stabilization, one obtains 28 kcal. as against 61 for benzene. It is known that full resonance is only possible for systems of olefinic carbon atoms lying in one plane, and, as double bonds are undoubtedly present, the resonance is reduced to an extent commensurate with the degree of deviation from the planar model.[46a]

Indeed, the double bonds are very largely olefinic. One can hydrogenate cyclooctatetraene catalytically and reach a break in the rate of hydrogen absorption after 3 moles of H_2 are added, especially in methanol and tetrahydrofuran; 4 moles, however, are absorbed eventually, and cyclooctane is the end product of the reaction. From the intermediary cyclooctene, suberic acid, an interesting dicarboxylic acid, can be prepared in the normal manner.

It is characteristic for a system of this type that it adds two atoms of alkali metal at the end of one of the diene systems. The addition product, upon hydrolysis, gives cyclooctatriene-(1,3,6). Furthermore, cyclooctatetraene is capable of di- and polymerization. Two dimerides, one a solid, the other a viscous oil, are obtained upon heating, the former containing three, and the latter two, double bonds. In the presence of air only the liquid dimeride is formed. Their structures are not clear, but one has tried to formulate the liquid dimeride on the basis of an assumption for which another interesting type of reactivity has to be considered. In many reactions the molecule of cyclooctatetraene shows the ability to rearrange either into a cyclohexadienocyclobutene (bicyclo[0,2,4]octatriene-(2,4,7)) or into a tricyclic system consisting of a cyclohexadiene and two cyclopropane rings (1,2,4,5-dimethylene-2,5-cyclohexadiene).

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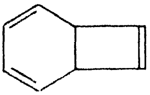
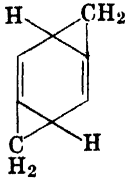
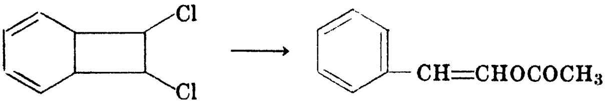
[46] See also Maccoli, *Nature*, 157, 695 (1946).

[46a] The presence of a conjugated cyclic system is indicated by the diamagnetic susceptibility. Pink and Ubbelohde, *Nature*, **160**, 502 (1947).

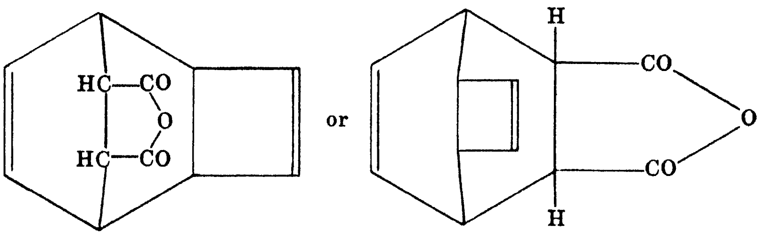




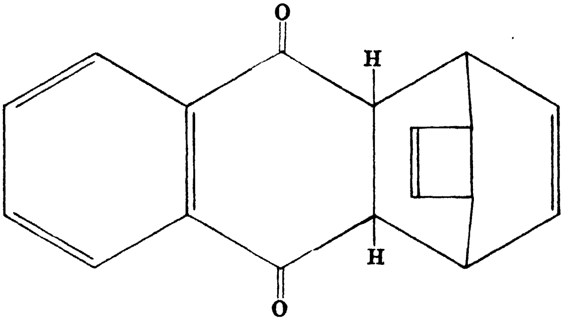
The former can isomerize to the system of ethylbenzene. A very clearcut example is the isomerization of the epoxide of cyclooctatetraene, which in the presence of a trace of acid isomerizes to phenylacetaldehyde with great violence. Other reactions are more complicated. All oxidations are accompanied by ring isomerization—we have just seen that in the end even the very mild perbenzoic acid has this effect. Vapor phase oxidation with air in the presence of vanadium pentoxide as catalyst gives benzoic acid; permanganate gives the same acid together with benzaldehyde. Hypochlorous and chromic acids, on the other hand, react—at least to some extent—with the tricyclic form of cyclooctatetraene; they give terephthaldialdehyde and terephthalic acid, respectively. On the whole, the isomerization to the cyclohexadienocyclobutene system is favored; the derivatives of this system are formed in all halogenation and all Diels-Alder reactions of cyclooctatetraene. Chlorination and bromination lead successively to di-, tetra-, and hexahalides; the last-mentioned ones are fully saturated. This already points to the bicyclic system which contains three double bonds. An exact proof for the structure of $C_8H_8Cl_2$, was established in the following way. Through the diacetate, it can be converted by hydrogenation (with four atoms of hydrogen) and saponification into a crystalline glycol, $C_8H_{14}O_2$, which upon oxidation gives *cis*-hexahydrophthalic acid. This shows that one of the rings in the dichloride is six-membered and that the second one is linked to it through two neighboring ring atoms; it must therefore be four-membered. It shows further that the two chlorine atoms are located in that four-membered ring; otherwise, the hydroxyl groups would have appeared in the molecule of the dibasic acid. The structure is further supported by the observation that the dichloride gives styryl acetate with hot glacial acetic acid:



Only one molecule of dienophilic reagents is added by cyclooctatetraene, and even for this first molecule a relatively high condensation temperature (100°) is required. Again, it could be proven that this is due to the fact that the cyclooctatetraene reacts in its bicyclic form which does not possess more than one conjugated system. The derivative obtained with maleic anhydride would then be:

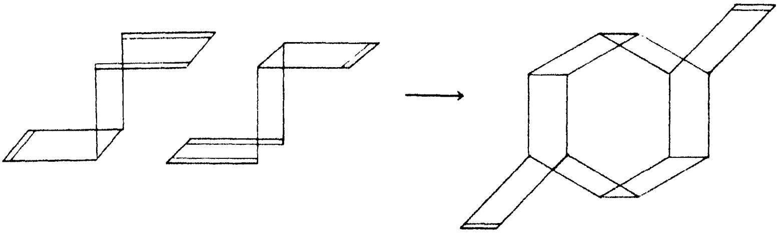


and indeed it gives all the reactions expected from such a substance. An interesting and very simple proof could be offered in the case of the reaction with naphthoquinone. The product which is formed:



loses hydrogen easily and C_4H_4 at a higher temperature and gives anthraquinone. One would hardly expect cyclobutadiene to be isolated under these conditions; and, indeed, only resinous products were observed.

Let us return now to the dimerization of cyclooctatetraene. One can understand that a dimeride—the liquid one—with two double bonds is formed, if one assumes the following tridimensional reaction of the bicyclic form:



One obtains a six-sided prism, a layer polymer. It is interesting that a similar reaction has been known, *viz.*, the photochemical dimerization of anthracene,[47] in which the two molecules form a tridimensional structure held together by formal valencies in the 9 and 10 positions. This constitutes an unusual type of polymer. The solid dimer, which has three double bonds, might equally owe its formation to a combination of the bicyclic and the tricyclic forms of cyclooctatetraene, for example:

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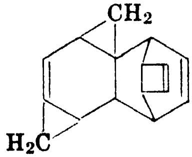
[47] Fritzsche, *Z. Chem.*, 3, 289 (1867); 5, 387 (1869).



Indeed, the study of cyclooctatetraene opens new vistas in many respects, and even if its technical importance might not be as great as one would have assumed—it does lead to suberic acid and phenylacetaldehyde, however—it is a gold mine for the theoretician.

There are a number of reactions of some complicated acetylene derivatives for which this is equally true. Let us take as an example phenylpropiolic acid. It shows all the normal reactions of an acetylene derivative; it adds catalytically activated hydrogen in the *cis* position,[48] whereas chemical reduction leads to *trans*-cinnamic acid.[49] Its esters and the nitrile easily add alcohols,[50] phenols,[51] amines,[52] and also hydrogen cyanide,[53] so that the hydrogen adds to the terminal, the remainder of the reagent molecule to the internal acetylenic carbon atom. A very strong intramolecular addition reaction is exhibited by *o*-nitrophenylpropiolic acid.[54] Its ester is isomerized by concentrated sulfuric acid to that of isatogenic acid:

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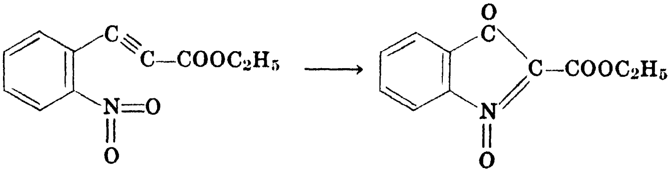
[48] Paal and Hartmann, *Ber.*, 42, 3920 (1909). Paal and Schwarz, *ibid.*, 51, 640 (1918).

[49] Aronstein and Holleman, *Ber.*, 22, 1181 (1889). E. Fischer, *Ann.*, 386, 385 (1912); 394, 361 (1912).

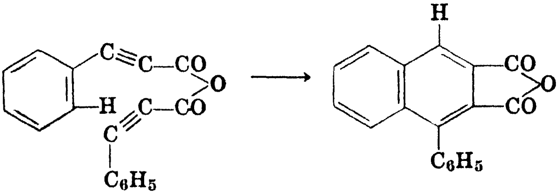
[50] Moureu and Lazennec, *Bull. soc. chim.*, 35, 526 *et seq.* (1906).

[51] Ruhemann and Beddow, *J. Chem. Soc.*, 77, 984 (1900). Ruhemann, *Ber.*, 46, 2194, 3386 (1913); 47, 120 (1914). Bogert and Marcus, *J. Am. Chem. Soc.*, 41, 87 (1919). Moureu and Lazennec, *Bull. soc. chim.*, 35, 526 *et seq.* (1906); *Compt. rend.*, 142, 894 (1906).

[52] Moureu and Lazennec, *Bull. soc. chim.*, [3] 35, 526 *et seq.* (1906); 35, 1179 *et seq.* (1906); *Compt. rend.*, 143, 596 (1906). Ruhemann and Cunnington, *J. Chem. Soc.*, 75, 956 (1899).



As you know, this is the path of the classical first indigo synthesis. But an unusual, new type of reaction is shown by phenylpropiolic acid and its substitution products, if they are treated with anhydrizing agents such as acetic anhydride or phosphorus oxychloride.[55] The anhydride is formed, and the two triple bonds in the latter are brought into such close proximity that they add to each other to form a naphthalene derivative, thus:



A similar case has recently been described by Nazarov.[56] In the presence of acids the (vinylethynyl)-dialkylcarbinols are first etherified and then cyclized to tetraalkylvinylisocoumaranes:

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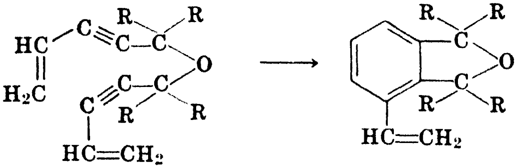
[53] Cobb, *Am. Chem. J.*, 45, 604 (1911).

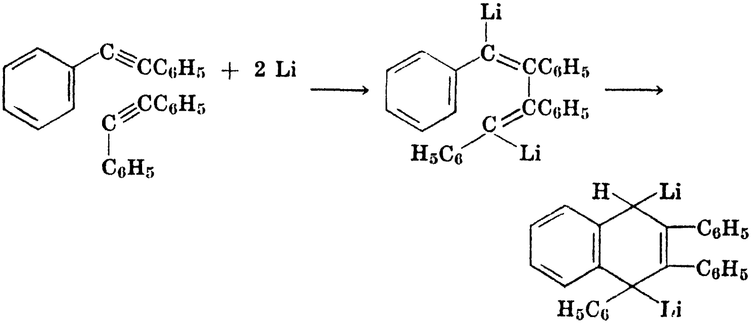
[54] Baeyer, *Ber.*, 14, 1741 (1881).

[55] Michael, *Ber.*, 39, 1909 (1906); *Am. Chem. J.*, 20, 89 (1898). Lanser, *Ber.*, 32, 2478 (1899).

[56] Nazarov and Verkholetova, *Chem. Abstracts*, 36, 1296 (1942); 37, 2343 (1943).



Analogously in the investigations of Schlenk[57] on the behavior of unsaturated phenylated compounds against alkali metal, tolane has been shown to react as follows:



All these reactions are not without analogy in the frame of the experimental material discussed in this seminar. In the last case, of course, the two acetylenic systems are brought together through a real link created by the one-sided addition of the alkali metal to the diphenylacetylene.

Another case which deserves mention because of its theoretical interest is that of (phenylethynyl)-diphenylcarbinol, the product which is obtained by the normal condensation of phenylacetylene and benzophenone.[58] If its chloride is heated, it loses hydrochloric acid and is converted into rubrene, a hydrocarbon which has been identified as 9,10,11,12-tetraphenylnaphthacene.[59] Its formation is best pictured as follows:

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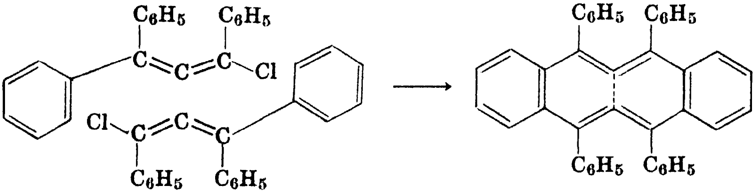
[57] Schlenk and Bergmann, *Ann.*, 463, 76 *et seq.* (1928). E. Bergmann and Zwecker, *ibid.*, 487, 156 *et seq.* (1931).



The dibenzocyclohexadecaene formed primarily stabilizes in an easily understandable manner—and thus we revert to that interesting new class of highly unsaturated cyclanes which have become available.

It might be an apt conclusion to these considerations if we refer to the very little known fact that a certain number of acetylene derivatives occur in nature—surely the organic chemist would not have thought that possible in view of the high reactivity of the acetylene system.

Pfau and his co-workers[60] isolated from the roots of *Carlina acaulis* an oxygen-containing substance called carlina oxide which has the formula of a 1-furyl-3-phenyl-1-propyne. The Raman spectrum has the lines of 2037 and

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[58] Wittig and Witt, *Ber.*, 74, 1474 (1941). See also Wilson and Hyslop, *J. Chem. Soc.*, 123, 2612 (1923).

[59] Dufraisse and Velluz, *Compt. rend.*, 201, 1394 (1935); *Bull. soc. chim.*, 3, 1905 (1936). Allen and Gilman, *J. Am. Chem. Soc.*, 58, 937 (1936). Dufraisse and Compagnon, *Compt. rend.*, 207, 585 (1938). See also E. Bergmann, *J. Chem. Soc.*, 1938, 1147.

[60] Pfau, Pictet, Plattner, and Susy, *Helv. Chim. Acta*, 18, 935 (1935).

2233 which are characteristic for all acetylenes, and a synthesis of the tetrahydro derivative (1-furyl-3-phenylpropane)[60a] supports the formula.

It is perhaps still more interesting that among the many unsaturated fatty acids there is one, $C_{18}H_{32}O_4$, which undoubtedly has the normal skeleton of stearic acid and a triple bond in a rather unusual position. It is the so-called Tariri acid[61] which was isolated in 1892 from Tariri seeds, originating in an oil-bearing plant occurring in Guatemala, and from the seeds of *Picrammia lindeniana.* Hydrogenation gives stearic acid, while hydration gives a ketostearic acid. The location of the triple bond follows unequivocally from the permanganate oxidation which gives adipic acid, $HOOC(CH_2)_4COOH$, and lauric acid, $CH_3(CH_2)_{10}COOH$.

Another fatty oil, of African origin, that of *Ongokea klaineana*—which is a quick-drying oil—contains together with oleic acid and linoleic acid a rather unstable acid,[62] which is conspicuous because of the fact that it is solid (at 10°C.), a property which it shares with Tariri acid. It is also a C_{18} acid and oxidation, or rather ozonization, of its ethyl ester leads to the monoester of azelaic acid, adipic acid, oxalic acid, and formaldehyde. They can be accounted for by the formula:

$$CH_2{=}CH(CH_2)_4C{\equiv}CC{\equiv}C(CH_2)_7COOR$$

The two conjugated triple bonds express themselves in the exaltation of the molecular refraction—this is a criterion we have discussed before—and they are undoubtedly also the reason for the good drying properties of the oil. It may be useful to add that the formula is not quite unequivocal; the structure:

[60a] Gilman, Van Ess, and Burtner, *J. Am. Chem. Soc.*, **55**, 3461 (1933).

[61] Arnaud, *Bull. soc. chim.*, 7, 233 (1892). See Grimme, *Chem. Rev. Fett- u. Harz-Ind.*, 19, 51 (1912); *Chem. Zentr.*, 1912, I, 1125.

[62] Sörensen and Stene, *Ann.*, 549, 80 (1941). Compare Castille, *Chem. Abstracts*, 41, 3049 (1947) ("erythrogenic acid").

$$CH_2{=}CHC{\equiv}C(CH_2)_4C{\equiv}C(CH_2)_7COOR$$

would be equally satisfactory and the conjugation would be that between a double and a triple bond. As we have seen before, it would be possible to decide between the two formulae on the basis of the absolute value of the extinction coefficient.

In view of what we have learned in comparing the properties and reactivities of the acetylenic and the ethylenic systems, it is perhaps not more surprising to find such substances in nature than to find the corresponding olefins or dienes. Very probably, the plants contain substances which inhibit the obvious attack of oxygen on such systems. Thus, once more, the theoretical conclusions at which we have arrived prove of some value even from the point of view of the biochemist.

We have arrived at the end of our way, although it lies in the nature of organic chemistry that such an end is always artificial. Indeed, from the point of view of somebody who is—as it is today the fashion—more interested in the theoretical aspects of chemical phenomena, such a survey as we have tried to give must seem unsatisfactory; but I believe that even to him the mere accumulation of experimental material must be of value as a prerequisite for the theoretical understanding of the field. And I hope I have achieved that: to show that here is a field which represents some questions and answers and which promises to respond generously to the labors of the organic chemist. If our discussion will stimulate you to research in this domain, the object of these seminars which you have followed with so much attention has been achieved.

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